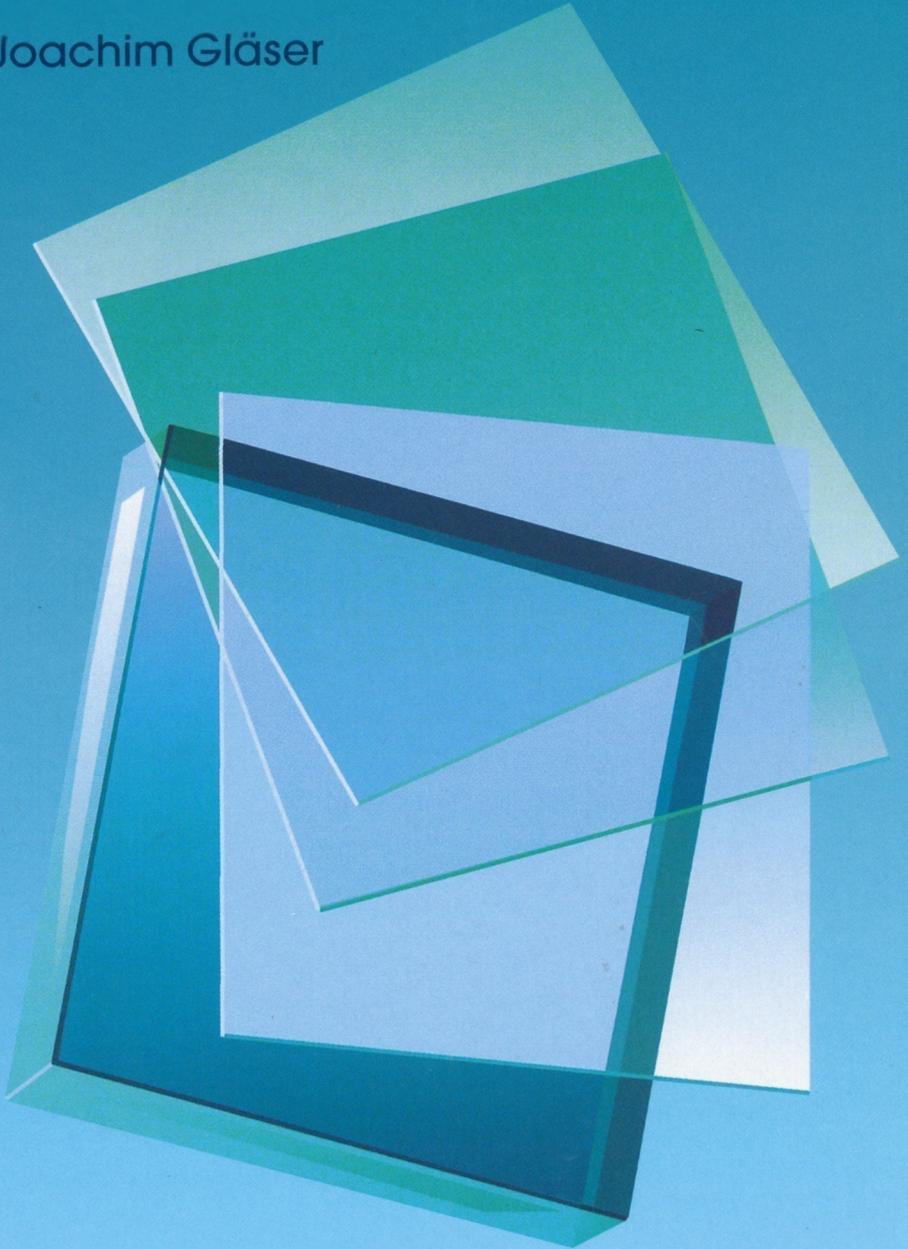


Thin-Film Technology on Flat Glass and Applications

Hans Joachim Gläser



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Part I

- Flat glass as a material
- Definitions
- The surface of flat glass
- Thin-film coating technologies for flat glass



Glass goblet with a decorative enamel coating with the name of Pharaoh Thutmose III in the cartouche (from about 1450 B.C.)

Soon after the invention of glass as a material, artisans learned how to refine it by coating.

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Foreword

This E-book is based on the English manuscript, „Large-Area Glass Coating“, which was the basis for translation and publication of a book of the same title in Chinese by the Ardenne Anlagentechnik company in Dresden, Germany. It was improved in various places and brought up to date (2015) by the author as far as possible.

The author thanks the Interpane AG company and employees of the Interpane Entwicklungs- und Beratungsgesellschaft mbH company in Lauenförde, Germany, particularly Dr Lothar Herlitze and Kerstin Sorby, for financial support and expert assistance in preparing this E-book, as well as Dr Helen Rose Wilson from the Fraunhofer Institute for Solar Energy Systems ISE in Freiburg, Germany, for the committed help to translate the German text into English. My thanks also go to my daughter, Stephanie Sahl, for designing the cover.

Hans Joachim Gläser

Gummersbach, January 2016

1 Flat glass

1.1 A short history of flat glass

Glass is a very old artificial material, the earliest finds of which can be traced back to the 5th century B.C. However, it was not until the beginning of the first century AD that the Romans succeeded in manufacturing flat glass by casting. They poured the glass melt into a plane mould and smoothed it flat. By this process glass panes of up to 70 cm x 100 cm could be made. Yet details of this manufacturing process are not recorded. Once the blowpipe was invented, the Romans developed the cylinder blowing process to produce flat glass — a method described by THEOPHILUS PRESBYTER in the *Schedula* in the early 12th century. Because flat glass production was still a difficult process and certainly quite expensive, the material was only used at that time for prestigious buildings such as the Forum Thermae or the imperial villas in Rome. But the Romans made significant progress in the craft of flat glass production and processing and quickly took it all over Europe, so that in the early Middle Ages, flat glass began to replace other transparent window materials. By then, many church windows, for example, were made from flat glass. Glass manufacturers were called 'vitrearii' by the Romans ([Lat.] *vitrum* = glass). They supplied their glass lites to 'speculariarii', the window makers, to be made into window panes.

Other types of window glass, such as bull's eye panes and glass roundels, are also medieval inventions. In the 17th century, cast glass, which was developed and produced by LUCAS DE NEHOU in St. Gobain (France), expanded the flat glass product range. In order to manufacture mirror glass, raw cast lites had to be polished – a very expensive and laborious process. But without the development of this technique the magnificent Palace of Versailles near Paris (erected 1661–89), for example, would never have been decorated with all its impressive mirrors.

Around the middle of the 19th century the first experiments were made with continuous machine-drawing technologies for the production of flat glass. These efforts were eventually successful, resulting in the Fourcault Process and the Colburn Process which were both developed in the early 20th century. The companies Pittsburgh Plate Glass (PPG) in the USA and Asahi in Japan derived refined production technologies from these processes in the 1920s. Flat glass made by drawing processes is called machine-drawn flat glass, previously known as sheet glass. For use today, however, these types do not have any mirror glass qualities.

It was only after World War II that the British company Pilkington manufactured high-quality continuous glass ribbons by allowing the glass melt to float on molten metal. Although the idea of this technology was not new then, Pilkington was the first company to succeed in producing float glass on an industrial scale. Today, flat glass made using float technology has become the most common type. However, other types of flat glass are still manufactured, but in smaller quantities. For example, machine-drawn glass or panes, produced using essentially the same cast-roll technologies as were designed back in the 19th century, are still made, mainly as ornamental or wire-reinforced glass. Smaller quantities of flat glass are also produced with still older processes. Chemically, all these flat glass types belong to the 'soda lime glass' group.

The coating of flat glass has been documented since the Middle Ages. THEOPHILUS PRESBYTER'S *Schedula* provides the first evidence of coating flat glass panes with black stain, an early form of enamel paint, to be used for church windows, for example. From the 16th century onwards, flat glass was coated with metal layers in order to make mirrors. Industrial-scale metal coating started in about the middle of the 19th century with the production of silver-coated mirrors. The industrial coating processes were expanded, leading to laminated sheet glass production and ceramic paint coating (enamelling) in the early 20th century. All the coating processes mentioned result in thick film coatings. After World War II, however, the development of the flat glass thin film coating processes, which are dealt with in this book, advanced rapidly. This promoted and increased both the popularity and number of applications of flat glass as a construction material.

1.2 Float glass

The European standard EN 572-1 defines float glass as

Flat, transparent, clear or tinted soda lime silicate glass having parallel and polished faces obtained by continuous casting and flotation on a metal bath.

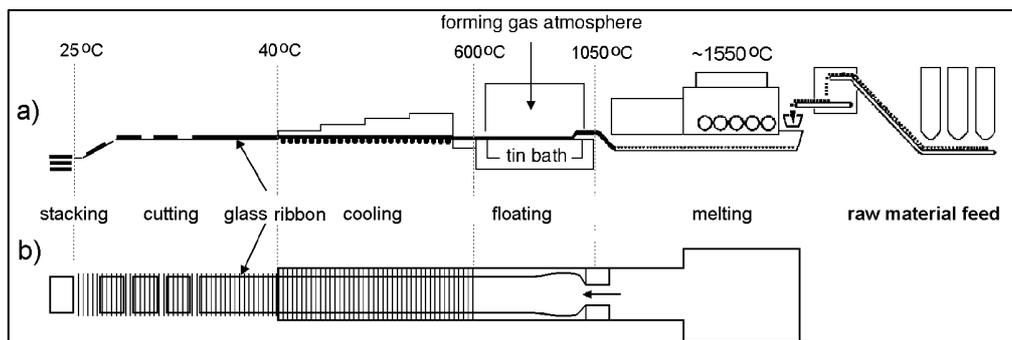


Figure 1.2.1: Design of a flat glass production plant using the float process
a) side view b) top view

With this technique, the glass panes are shaped in a reducing atmosphere as the glass melt is poured onto a shallow tin bath where it floats and spreads flat and evenly, due to its surface tension. This ensures that the glass panes have extremely parallel and even surfaces resulting in a product which is transparent and without distortion to match today's quality requirements for mirror glass. Today, float glass panes are generally produced up to a size of 3.21 m x 6.00 m; known in the industry as the 'jumbo size'. Typically, float glass ranges from 3 to 19 mm in thickness. Technically, it is possible to produce panes of thicknesses ranging from less than 1 mm to 25 mm. The pane thickness is determined by the transportation velocity of the glass ribbon and the flow of the molten glass onto the tin bath, but also by stretching the glass ribbon (for a pane less than 6 mm thick) or compressing it (for a pane more than 6 mm thick) at its edges in the float bath zone. The surface evenness, technically called 'planeness', is often a key quality criterion when it comes to coating processes. The planeness is mainly controlled by the homogeneity of the glass melt, the

shaping process, i.e. stretching or compressing the edges of the pane in the floating zone, and the cooling process the glass ribbon undergoes after shaping.

The requirements regarding the size and quality of float glass to be used as construction material, especially concerning visible and optical flaws relevant to coating, are set out in DIN EN 572-2 together with conditions for testing and acceptance. For the flat glass coating expert, however, specific requirements have to be met regarding planeness and surface conditions, e.g. corrosion¹. Such additional characteristics are not yet set out in an industrial standard and therefore must be agreed with the flat glass manufacturer individually. In some cases, a maximum geometric deviation allowed from a determined reference edge is specified analogously to EN 572-2 as the planeness quality requirement for panes to be coated. Generally, a distinction is made here between short wave and long wave deviations. With flat glass panes intended for optoelectronic applications, the short wave deviations are of particular significance: E.g. $\leq 0.7 \mu\text{m}/\text{cm}$ might be the deviation limit for this purpose (see explanation in Chapter 6.1.1, Part II). The problem of flat glass surface corrosion is dealt with in Chapter 3.2 in some detail.

It should be pointed out that borosilicate glass is now also produced using the float process. This type of flat glass is mainly used as fire-proofing material, in oven doors for instance, or as a special material in a number of products for which soda lime glass cannot be used.

1.3 Chemical composition and structure of flat glass

Flat glass in modern use is almost exclusively float glass and belongs to the category of soda-lime glass. It is made from natural materials (quartz sand, lime, dolomite and feldspar or nepheline syenite) and synthetic materials (soda and sulphate and a considerable proportion of waste flat glass). Flat glass is a recyclable material. Since flat glass manufacturers demand high quality from the raw materials, these must be worked, treated and produced carefully.

compound	chemical formula	mass proportion (weight %)
silicon dioxide	SiO ₂	72.8
calcium oxide	CaO	8.6
sodium oxide	Na ₂ O	13.8
magnesium oxide	MgO	3.6
aluminium oxide	Al ₂ O ₃	0.7

Table 1.3.1 Chemical composition of float glass

¹ An excellent review of modern optical flat glass quality measuring technologies is given in the brochure "Glass, Edition II", edited by *Verband Deutscher Maschinen- und Anlagenbau e.V., Frankfurt (Germany)*, 2002.

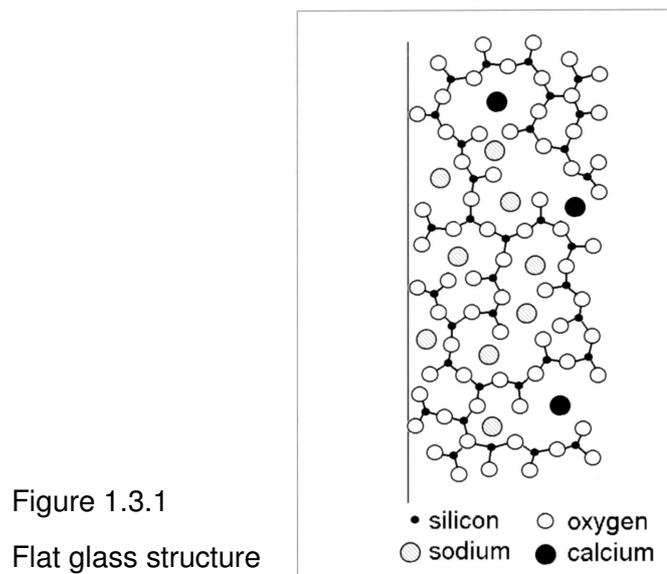
The basic materials are available in almost infinite quantities all over the world. The production of 1 kg flat glass requires approximately 4.0 kWh of energy as opposed to about 10.5 kWh needed per kilogram of construction steel. This is due not least to the material and energy-saving utilisation of recycled glass. The typical chemical composition of float glass is shown in Table 1.3.1.

Flat glass may contain additional compounds, such as iron oxides, according to the source and quality of the raw materials. Coloured panes are made by adding inorganic tints during the melting process (see Chapter 1.4.1).

The composition of standard float glass sold today is relatively uniform due to standardised composition and production processes. Alterations to the chemical composition have an impact on additional processing and on some characteristics such as resistance to climatic conditions. A higher proportion of Al_2O_3 , SiO_2 and CaO , for example, results in improved weather resistance, while a higher content of alkali oxides makes it more susceptible to climatic attacks. The art of flat glass production is to find and maintain the ideal composition, taking cost, requirements for additional processing and application into consideration. In the following sections, “flat glass” and “float glass” are used as synonyms.

When coating flat glass it is necessary to be aware of its high sodium oxide content. The sodium ion (Na^+) has a small radius and is therefore very mobile. Even at temperatures below 100°C it can diffuse noticeably into deposited layers, causing impurities and usually having negative effects. The Na^+ diffusion can be countered with special diffusion-blocking layers (see also Chapter 5.1.2.1).

As far as its structure is concerned, flat glass is like any ordinary glass, ‘an inorganic product of fusion which has cooled to a rigid condition without crystallizing’, according to the definition by the American Society for Testing and Materials (ASTM). Engineers speak of ‘frozen, supercooled liquids’. Figure 1.3.1 shows a diagram of flat glass structure.



In Figure 1.3.1, one can clearly see the short-range order surrounding the silicon (Si) atoms in the form of SiO_2 molecules which, in turn, are bound in an irregular network. Hence, SiO_2 is also called a network-generating substance. The SiO_2 network is broken up irregularly by network converters, i.e. by the embedding of sodium (Na^+) and calcium (Ca^{2+}) ions which

have been added to the melt as soda and lime. This structural order is similar to that of liquids, although glass is a solid material under normal conditions. Solids are usually characterised by the regular ordering of their atoms in crystal lattices, i.e. they have a wide-range order. This structural order of matter is known as “crystalline”, whereas the structural order encountered in glass is “non-crystalline”. The composition and structure are the main factors which influence the properties of flat glass.

As far as its ecological impact is concerned, flat glass is a chemically inert material and so is completely harmless to the environment.

1.4 Properties of flat glass

1.4.1 Optical properties

The most outstanding property of flat glass is its high transmittance of solar radiation. This is due to the fact that glass is an electric insulator and that it absorbs practically no solar radiation except in the UV and near infrared wavelength ranges. Because of the low but significant content of ferrous and ferric oxides in the natural raw materials (approximately 0.1 wt.%), the absorption of near infrared radiation, particularly around the wavelength of 1.15 μm , is increased (see also Figure 1.4.1.1). This is why standard flat glass appears greenish in colour. The latter effect can be observed particularly clearly when looking at the cut edge of a pane.

Using raw materials with an iron content of one tenth of that for standard glass results in “white” or “low-iron” glass, which has lower absorptance and increased transmittance of solar radiation. These “white” glass types (e.g. ‘Diamant’ made by Saint-Gobain, ‘Optiwhite’ made by Pilkington or ‘ipawhite’ made by Interpane) are also produced using the float technology; and there looks to be a future for them in various applications, such as the conversion of solar radiation into thermal energy or electricity.

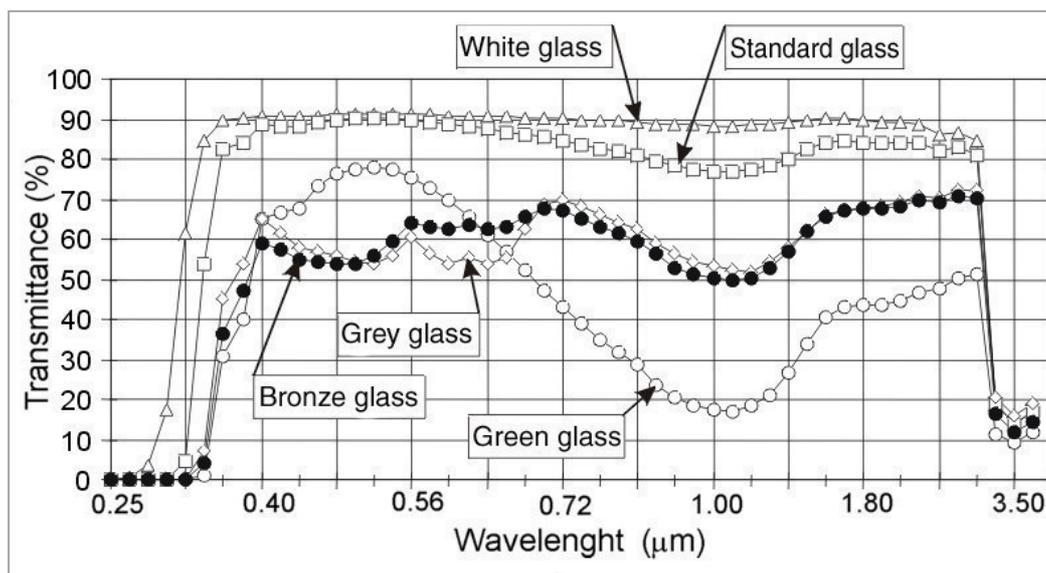


Figure 1.4.1.1 Spectral transmittance of various 4 mm-thick float glass types in the solar range

On the other hand, metal oxides may be added to the melt to make tinted glass, the solar transmittance of which is lower than that of standard glass. The most frequently used tinted glass types are grey, bronze or green glass such as 'Parsol grey, bronze and green' made by Saint-Gobain and 'Optigrey, Optibronze and Optigreen' made by Pilkington. Whereas iron oxides are added to make green glass, a combination of nickel, cobalt and iron compounds is used for grey glass, and cobalt, iron and selenium compounds are used for bronze glass. Figure 1.4.1.1 compares the transmittance spectra of 4 mm-thick white and standard float glass with those of green, bronze and grey float glass for the entire solar radiation range.

Theoretically, the optical properties of flat glass can be determined by use of the refractive index n and the pane thickness d . Since standard flat glass and white glass absorb almost no visible light, their refractive index n in this range is 1.52. From this it follows that the light reflectance at each surface of either standard flat glass or white glass is about 4 % (for details see Chapter 5.1.1.2) and hence about 8 % for the entire pane. The entire light reflectance for tinted glass is lower according to its absorption.

1.4.2 Mechanical properties

The mechanical properties of flat glass, which are important for additional processing or when the glass is used as a building material, are compared with those of (construction) steel in Table 1.4.2.1.

property [unit of measurement]	annealed glass	tempered glass (e.g. TSG)	steel *
density [g/cm ³]	2.5	2.5	7.8
tensile strength [N/mm ²]	30 ** - 100 ***	50 ** - 150 ***	360 - 510
compressive strength [N/mm ²]	700 - 900	700 - 900	1,440 - 2,040
modulus of elasticity [N/mm ²]	$7.3 \cdot 10^4$	$7 \cdot 10^4$	$2.1 \cdot 10^5$
scratch hardness [according to Mohs]	5 - 6	5 - 6	3.5 - 4.5

* ex works

** acceptable for calculation

*** measured value

Table 1.4.2.1 Mechanical properties of flat glass and steel

After the production process, flat glass is annealed. Glass is referred to as 'tempered' after it has undergone a toughening process, e.g. through the production process of Tempered Safety Glass (TSG). Compared with steel, it is noticeable that glass displays lower resistance to bending strength, but a higher abrasive hardness. The theoretical tensile strength of flat glass is about 6,000 N/mm², i.e. it is much higher than that of steel. However, surface micro-flaws, caused by handling procedures (such as on conveyor belts or during stacking or transportation) as well as by corrosion, result in lower measured values (up to 100 N/mm²). For safety reasons, the tensile strength is typically calculated with a value of 30 N/mm² when flat glass is used. The tensile strength of glass can be improved by toughening, e.g. through the TSG process.

Regarding its mechanical properties, it can generally be said that flat glass is a hard substance with a limited tensile strength; i.e. flat glass is a brittle material.

When coating flat glass it is essential to observe that every individual pane is under a certain compressive and tensile stress due to the after-shaping cooling process. This is collectively referred to as the permanent residual stress of flat glass. These stresses can have an impact on the subsequent processing stages of the flat glass. Figure 1.4.2.1 shows a measured curve of the permanent residual stress in the depth of a flat glass pane. Similar curves can be expected all over the pane surface, i.e. from one edge to the other of the drawn glass ribbon.

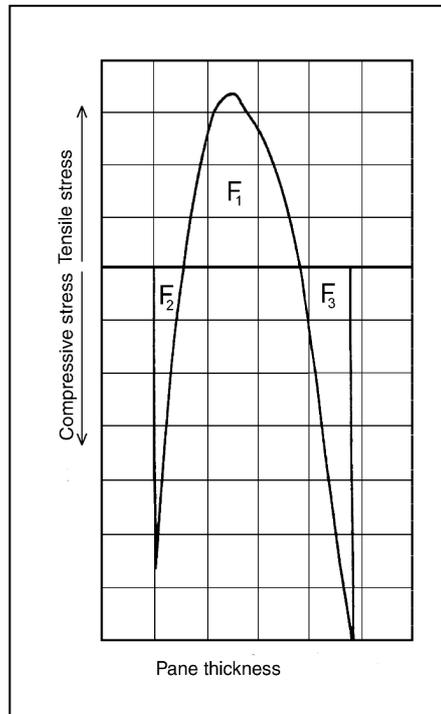


Figure 1.4.2.1
Sample stress curve across
the thickness of a drawn glass
pane (from Fourcault
production)

In Figure 1.4.2.1 it can be seen that there are two areas of compressive stress on the surfaces and an area of tensile stress in the centre of the pane. For balance, the area under the stress curve F_1 should equal the sum of the areas F_2 and F_3 . Ideally, these areas should be symmetrical with the median line of the pane. In reality though, the residual stress curve of a drawn glass ribbon runs differently from surface to surface and from edge to edge, depending on the cooling conditions. The task and the art of the flat glass manufacturer is to control the cooling process so that on the one hand the residual stresses remain low and on the other the remaining stresses in the cooled glass are equally distributed over the pane thickness and width. In general, the zones of compressive and tensile stress are no longer as pronounced for modern float glass as they were for earlier drawn glass.

1.4.3 Thermal properties

The structure of glass mentioned above also affects the melting point. Unlike crystalline substances, glass does not have a defined melting point; rather there is a temperature at which the material starts to soften (T_g point). This temperature varies between 550°C and 600°C for typical flat glass. Further thermal properties of flat glass which are relevant for its application are shown in Table 1.4.3.1, again in comparison with construction steel.

From Table 1.4.3.1 it can be seen that the thermally induced linear expansion of flat glass is similar to that of steel, whereas its thermal conductivity is much lower. Furthermore, it is

significant that flat glass does not resist temperature changes well. This property can be improved by toughening, e.g. by means of the TSG process.

Even small temperature changes within a large pane may cause considerable warping due to unequal thermal expansion. For small panes, as are used in laboratory-scale experiments, warping is irrelevant. However, when coating large panes which have been pre-heated inhomogeneously or are unevenly heated during the coating process on an industrial scale, warping can easily become a crucial criterion for the feasibility of the coating process as a whole.

property [unit of measurement]	annealed glass	tempered glass (e.g. TSG)	steel*
coefficient of linear expansion at 20–300°C [K ⁻¹]	9.0 10 ⁻⁶	9.0 10 ⁻⁶	1.2 10 ⁻⁵
coefficient of thermal conductivity [W/mK]	1.0	1.0	50
resistance to temperature difference [K]	40	100	N/A
max. temperature to be used [°C] short-term	300	200	N/A
long-term	200	200	N/A

N/A = not announced * ex works

Table 1.4.3.1 Thermal properties of flat glass and steel

1.4.4 Electrical properties

Flat glass is an electrical insulator. Its resistance decreases as the temperature increases, but not substantially. It is only above the softening point that resistance drops faster, due to ion conduction. Values of the most important electrical properties of flat glass are displayed in Table 1.4.4.1.

property (unit of measurement)	symbol	estimated value	remarks
electric resistance [W*cm]	ρ	10 ¹⁰ -10 ¹¹	at 20 °C
dielectric constant	ϵ	7 - 8	
dissipation factor	tg δ	0.008 - 0.26	for 50 Hz
breakdown voltage [kV/cm]		450	for 50 Hz

Table 1.4.4.1 Electrical properties of flat glass: estimated values

(source: GOERK)

1.4.5 Chemical resistance

The resistance of flat glass to chemicals is of major importance, because it affects the pane surface and thus the coating process. Climatic resistance during storage and transportation as well as resistance to cleaning agents are of particular interest. In Chapter 1.3 it has already been pointed out that the weathering resistance of soda lime glass can be improved by increasing the SiO₂, Al₂O₃ and CaO content and/ or by decreasing the Na₂O content.

When evaluating chemical resistance, the following distinctions are made:

- resistance to acids, in accordance with DIN 12 116
- resistance to lyes, in accordance with DIN ISO 695
- resistance to water, in accordance with DIN 52 296

Since the chemical composition of flat glass produced in different glassworks does not diverge noticeably, products are also usually comparable with regard to their chemical resistance. According to the above standards, they can be classified as follows:

- Group 1 (excellent) with regard to resistance to acids (with the exception of hydrofluoric acid and hot phosphoric acid)
- Group 1 - 2 (good) with regard to resistance to lyes
- Group 3 - 4 (satisfactory) with regard to water resistance.

Under typical climatic conditions and chemical attacks, all flat glass types are considered to be durable in all their many applications. However, films of water remaining on the flat glass surface rapidly cause corrosion. The air humidity during production and subsequent storage thus has an appreciable effect on corrosion. As a result, flat glass is significantly more susceptible to corrosion in summer than in winter. Measures should be taken to prevent the temperature falling below the dew point during storage and transportation. Care must also be taken when cleaning the panes (see Chapter 3.4).

Corrosion causes leaching of the glass surface. In an advanced phase, a gel-like layer forms, the so-called corrosion layer (see also Chapter 3.2), which makes additional refinement such as coating difficult or even impossible. Therefore, the level of corrosion on the flat glass surface must be carefully observed for the application of a number of coatings. If the panes remain moist for an extended period, e.g. due to temperatures falling below the dew point while the panes are stored in stacks or because of leaky edge seals of insulating glass units allowing humid air to enter into the airspace, the pane surface can be etched by concentrated sodium hydroxide (NaOH) in the water film – a substance which is generated during the corrosion process of the glass surface.

It is important to know that after installation, e.g. in windows, glass corrosion starts on the outside surface due to the climatic conditions (rain or condensed water), but the sodium hydroxide which arises is diluted and removed permanently by continuous renewal of the water film by rain. Eventually, the generation of a corrosion layer comes to a standstill. In this case the layer does not usually have a negative effect; on the contrary, it conserves the outer surfaces of the glass. However, glass in this condition can no longer be coated.

1.5 Markets for flat glass

The major markets for flat glass today are:

- the building industry
- vehicle manufacturing
- the furniture industry

- interior decoration including mirror production
- energy technology (photovoltaics and solar thermal applications)
- display technology (e.g. flat screens for TV)

By far the largest share of manufactured flat glass is used in building products, followed by applications in vehicles. In the future, however, the most rapidly growing markets will be in the fields of power engineering, e.g. for solar energy conversion, and display technology.

In building construction, flat glass is used almost exclusively within advanced insulating glass units with two or more panes. All insulating glass units used in German façades today must comply with high thermal insulation requirements, as specified in the German 'Wärmeschutzverordnung' (Federal Thermal Insulation Directive). Only coated, thermally insulating glazing units can fulfil these requirements (see Section 5.1.3.1). In addition, the following type of glazing is used:

- solar-control glazing
- sound insulating glazing
- fire-protection glazing
- burglar-proof glazing
- decorative panes (e.g. ornamental glass, Georgian windows, bull's-eye panes or model panes)

As with the thermally insulating glazing, the functions of most of these special glass building products are achieved by the use of coatings.

Mirrors are made exclusively of coated float glass. Coated panes are becoming increasingly important for car windows. Coatings are also vital to the functionality of panes which are used in energy and display technology.

To summarise it can be said that

- Flat glass is a high-quality product which can be made inexpensively on a commercial scale from raw materials which are available everywhere in almost infinite supply.
- It is a recyclable and thus an environmentally friendly material.
- Flat glass possesses important properties, such as high transmission of solar radiation, sufficient hardness and high durability for most applications.
- Only a small proportion of the flat glass produced today is used as single panes without additional refinement.
- Today, flat glass is not a final product; rather it is a material from which high-quality refined products can be made.
- A large proportion of flat glass is refined by means of coating

2 Refining flat glass by means of coating

2.1 Classification of flat glass refinement processes

Flat glass refining processes comprise technologies through which the properties of the glass can be altered and new or different functions can be achieved. Refining increases the worth of flat glass. Different products can be developed and thus new markets can be opened up, leading to a higher worth added.

The individual refining processes can be categorised into four different groups:

- Processes to modify the pane form. Examples are bending, drilling and edge-grinding processes
- Processes to alter the glass matrix, e.g. thermal or chemical toughening
- Surface-treating processes, either subtractive (abrasion or etching) or additive (deposition). Coating processes belong to the latter sub-group
- Constructions made from flat glass by means of joining techniques, such as insulating glass units, façade elements, LCD displays, photovoltaic modules etc.

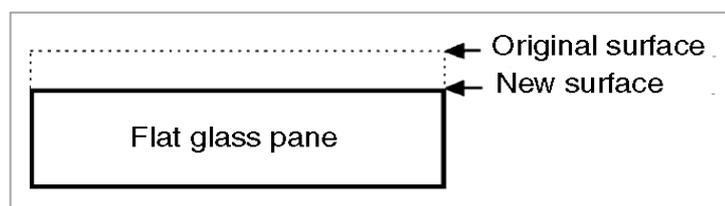
Increasingly, more than one refining process is employed for a single product; so that it is then known as multiply-refined flat glass. Insulating glass units, for instance, which has been used in vehicles for some years, represents the highest level of refinement. Technologies from all four of the above-mentioned groups are applied here: first, the panes are bent; secondly, they are toughened; thirdly, their edges are coated with an enamel to protect the edge seals from UV radiation and for some applications in premium cars, one of their surfaces is deposited with a solar control coating; and finally, by use of adhesive agents, pairs of panes are joined to make stepped insulation glass units.

2.2 Refining flat glass using surface-treating processes

As shown above, a distinction is made between subtractive and additive surface refining methods. All processes which generate a new surface inside the glass body belong to the subtractive group (see Figure 2.2.1).

Figure 2.2.1

Definition of subtractive glass surface refinement processes

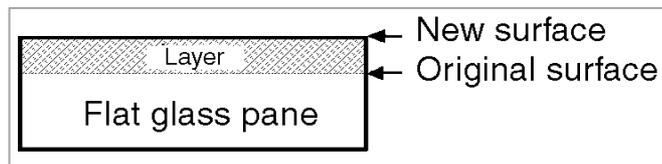


There are three main subtractive treatments for glass surfaces. One of these is etching, i.e. roughening the surface microscopically, for example, in order to make anti-reflection panes for picture frames or to create surface decoration. The second treatment is polishing, which is used to produce extremely plane surfaces for the manufacture of special mirrors or to remove layers of corrosion. Finally, grinding and sand-blasting processes are used to create surface ornamentation or to roughen the surface in a particular way, e.g. to produce frosted glass. Subtractive refinement will be discussed in this book only insofar as it competes with additive methods, as in the field of anti-reflection treatment (see Chapter 5.3.2).

The additive surface refinement processes include all treatments by means of which a new surface is generated outside the flat glass body by the deposition of material (see Figure 2.2.2).

Figure 2.2.2

Definition of additive glass surface refinement processes (coatings)



The additive surface refinement processes for float glass are the coating processes.

2.3 Coating processes and layers

Coating processes are production processes by means of which substrates are deposited with layers of different materials. In this case, the substrate is the large-area flat glass pane. The layers are characterised by

- a large-area which may also possess geometric structures, and
- strong adhesion to the substrate.

Materials which are deposited with weak or no adhesion to the substrate are known simply as coverings, the properties of which commonly differ from those of strongly adhering layers.

The adhesion of a coating to a substrate is achieved by adhesive forces at the interface between layer and substrate. The adhesion energy W_a serves as a measure for the adhesion of the layer. This is the energy necessary to separate two materials which are in contact (see also Chapter 5.5.1). According to MATTOX, adhesion is accomplished by intermediate layers, also known as interface layers. As shown in Figure 2.3.1, five types of interface layers are distinguished, each representing different adhesion mechanisms.

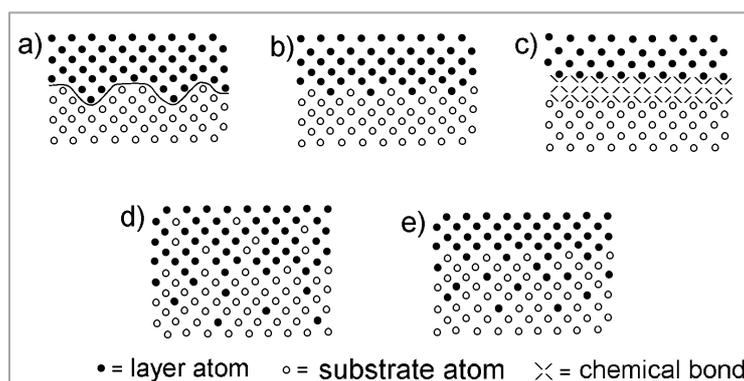


Figure 2.3.1 Diagram of the five types of interface layers between substrate and coating

(source: R. M. MATTOX; Sandia Lab Rep. SC-R-65-852, 1965)

Figure 2.3.1a) shows a mechanical anchor layer in which the deposited layer interlocks and so adheres due to the rough surface of the substrate. A classic example of this type of

interface layer is the adhesion of polyvinyl butyral (PVB) foil to glass for laminated safety glass.

Figure 2.3.1 b) shows an abrupt change from the substrate to the coated film within a few atom layers. In this case, the interface layers are about 0.2 to 0.5 nm thick and the adhesion to the glass surface is fairly weak. This adhesion mechanism is typical for films applied by thermal evaporation, or when there are impurities between the substrate and the layer.

Figure 2.3.1 c) shows an adhesion mechanism whereby the adhesion is achieved using a large interface layer created by chemical or metallic bonding between the substrate and the coating. The adhesion is very strong with this type of interface layer. Chemically deposited oxide layers on a glass surface often use this adhesion mechanism, for instance, with Si-O-Me bridges (see also at the end of Chapter 4.2.1.4).

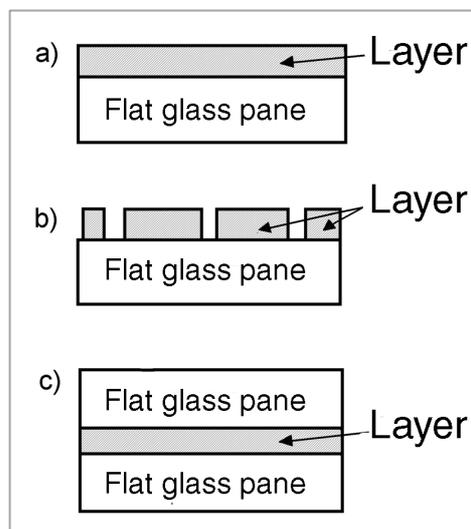
Figure 2.3.1 d) shows a diffusion interface layer which is the result of diffusing of materials into and out of the substrate surface. It is characterised by a decreasing concentration, i.e. a gradient of the coating material into the substrate and the layer. In order to generate such an interface layer, energy is needed, which can be supplied by heating the substrate or by ion bombardment. Usually, the adhesive strength of diffusion interface layers is high. This adhesion mechanism typically occurs with chemical depositions onto hot glass surfaces (see Chapter 4.3.2 and 4.3.3) or with sputtering processes (see Chapter 4.2.1).

Figure 2.3.1 e) shows a pseudo-diffusion interface layer. It is similar to the previous one, but differs insofar as there is only one gradient, the one from the deposit material into the substrate. Such interface layers result, for instance, from coating processes which involve implantation due to ion bombardment, also known as ion-plating. Ion implantation into the flat glass surface can also be observed with sputter depositions (see Chapter 4.2.1).

The five intermediate layers shown in Figure 2.3.1 represent ideal layer formations which in practice do not occur. Usually, a combination of a number of the above mechanisms leads to the adhesion. Chapter 5.5 in Part II deals with the adhesion of liquids or impurities to glass surfaces or coatings in more detail.

Figure 2.3.2 shows the general forms of layers on flat glass. The laminated glass (case (c) in Figure 2.3.2) is a borderline case of surface-treated flat glass, since it could also be classified as a joined flat glass product (belonging to the group of glass constructions, see above).

Figure 2.3.2
Forms of layers on flat glass
a) continuous coating
b) discontinuous coating
c) glass laminate



The application of layers can alter or add to the range of functions of flat glass. But, most importantly, drawbacks of flat glass (such as the risk of injury from panes broken due to the hardness and brittleness of glass, or the loss of transparency resulting from condensing humidity) can be compensated for.

The float glass properties which can be altered by means of coatings are grouped into

1) Optical properties

Transmittance, reflectance or absorptance

2) Electrical properties

Electrical properties and related functions such as thermal emittance

3) Mechanical properties

Glass fracture mode, improved sound insulation, improved dirt and water-repelling potential

4) Chemical properties

Barrier function to prevent e.g. sodium diffusion from the glass surface into coatings or block chemical attacks on the pane; and

5) Decorative properties

Modification and improvement of the glass finish or adaptation for special purposes.

Several functional changes can be achieved with a single coating. This is then called a multi-functional coating. Thus flat glass can be deposited with a coating which protects it from excess solar radiation, shields electromagnetic waves and reduces heat emission at the same time.

2.4 Flat glass coatings and their requirements

The coating processes for flat glass are classified as

- thin-film processes and
- thick-film processes.

The corresponding coatings are called thin-film or thick-film coatings. Formerly, the two coating types were distinguished in terms of their layer thickness. Coatings which were a maximum of 1 μm thick were called thin-film coatings and those which were thicker than 1 μm were called thick-film coatings. Today, a thick-film coating is identified thereby that the properties of the coating material and the bulk material of which it is made are the same. This is not the case for thin-film coatings, for which the properties vary with the coating thickness.

Typical processes for coating flat glass with thick films include those used to apply lacquers, resins, alkali silicates or foils deposited e.g. by spraying, brushing, casting, roller printing, screen printing etc., whereby in general the uniformity of the coating thickness applied plays only a minor role. Typical thin-film coating processes include those in which material is deposited in the vapour phase under vacuum condition or deposition occurs under atmospheric pressure from the vapour, liquid or solid phases. In these cases the uniformity of the uniformity of the coating thickness plays normally an important role.

The thin-film coating technologies applied to flat glass today and the resulting products form the subject of this book.

All flat glass coating processes must fulfil the following general requirements:

- 1) They must be suitable for use with flat glass as the substrate material. This means that the coating plants involved should not only be capable of coating, but also of handling (i.e. storing, conveying and positioning for coating) pane sizes up to 3.21 m x 6.00 m, so-called 'jumbo size'. It should be taken into consideration that flat glass is a brittle, at normal temperatures inflexible material with permanent residual stresses, which is furthermore hydrophilic and an electrical insulator. The fact is also often neglected that large area flat glass panes are very susceptible to warping, even with quite minor differences in temperature, and this can have a significant effect on the coating process and the layer properties. Extreme care is therefore necessary when coating large-area flat glass panes which are pre-heated or unevenly heated. In view of the many poorly-planned large coating plants which were built in the past, it seems essential to emphasise again that the substrate must be compatible with the coating plant and process.
- 2) The processes must be appropriate for use on large-area surfaces, i.e. the desired function must still be achieved on large-area surfaces. Laboratory-scale experiments are often unable to prove this.
- 3) The material to be deposited onto the glass surface, i.e. the coating material, must be compatible with the chosen process; it must be available in a form required by the process. Thus, for example, it is essential that the targets required for sputtering processes (see Chapter 4.2.1) in large plants can be produced and are functional. Again, not everything that works successfully in the laboratory can also be transferred to large plants.
- 4) Naturally, the processes used today must be environmentally friendly. Often, the chemical coating processes themselves are not. Usually, the plants have to be partly supplemented by very expensive facilities for the treatment of production materials and waste in order to comply with environmental requirements.
- 5) The processes must be economically viable, i.e. the cost-benefit ratio of the products must be acceptable to the market.

2.5 Interaction between the coating process, coating material and flat glass surface and the effect on the properties of the coating

The coating properties depend on

- the properties of the material to be coated (in this case the flat glass and here especially its surface),
- the coating material,
- the coating process.

All three of these factors can influence each other and thus have an effect on the properties and functionality of the coatings. This is illustrated by the following examples:

- **Interaction between the coating process and the coating material**
Coatings of the same material display different properties depending on the coating technique, e.g. depending on whether they are evaporated or sputtered in vacuum. The reason for this is the different growing conditions of the coatings during the coating process. If the coating conditions are not identical, even coatings of the same material and the same thickness deposited using the same process may differ when carried out at different plants.
- **Interaction between the coating material and the glass surface**
Thin gold and silver coatings, for instance, always start to grow in an insular fashion on a glass substrate. It is thus impossible to deposit very thin uniform coatings of these metals onto a glass surface. Unlike gold and silver, metal oxide coatings usually grow very homogeneously and uniformly from the first atom layers.
- **Interaction between the glass surface and the coating process**
For instance, when a conventional sputtering process is used, oxygen is released from the glass surface through ion bombardment. It is therefore extremely difficult to produce very thin, oxygen-free metal layers on flat glass using this technique. This is achieved much more easily with thermal evaporation processes, because highly energetic atoms, ions or molecules do not attack the glass surface in this case.

The conclusion can thus be drawn that, in order to create a coating with a particular function on a certain substrate (in this case the flat glass), the properties of the substrate and its surface, those of the coating material and of the coating technique and the interactions between them, must all be considered and co-ordinated.

The properties of the flat glass surface are of considerable importance for all coatings and coating processes. Therefore, this is the subject of the next chapter.

3 Glass surface condition and its effect on coatings

If the coating process is not integrated into the flat glass production process itself, the condition of the pane surface immediately before coating depends on:

- the properties of the original surface after forming
- surface corrosion (which was mentioned briefly in Chapter 1.4.5)
- deposited impurities.

These three factors and the effects of each one on coating processes will be explained and possible methods of preparing the flat glass for the coating processes will be shown below.

3.1 The original flat glass surface

The glass surface is formed during the shaping process, so physical processes and chemical reactions (particularly with the atmosphere) during forming and cooling have a significant effect on the properties of the glass surface. Figure 3.1.1 shows the most important of these physical effects and chemical reactions.

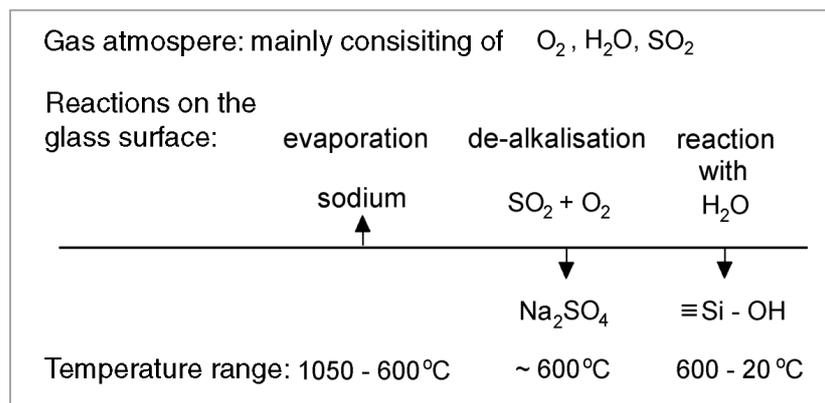


Figure 3.1.1 Important physical processes and chemical reaction on the flat glass surface during shaping and cooling

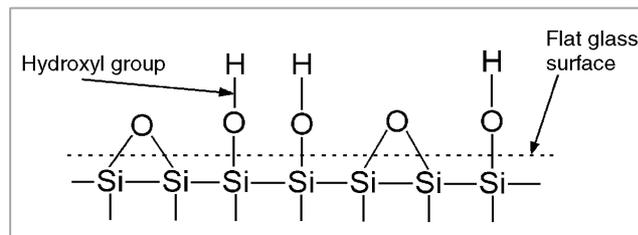
The most important effects and reactions are:

- Sodium evaporation – mainly as sodium oxide (Na_2O) or sodium hydroxide ($NaOH$) – resulting in the glass surface having a lower sodium content than the glass body. In the float glass production process, sodium compounds evaporate in the floating zone at temperatures of 1,050°C to about 600°C (see Figure 1.2.1).
- De-alkalisation in the cooling zone at temperatures of around 600°C, especially with sulphur dioxide (SO_2) which is added to the atmosphere in the cooling zone. During this process, the sodium in the glass surface reacts with atmospheric oxygen in the cooling zone and the SO_2 which is introduced there, leading to a further reduction of the sodium content in the glass surface. The product of this reaction, sodium sulphate (Na_2SO_4), is deposited onto the surface, where it acts as a lubricant for the transportation of the glass over conveyor rollers in the cooling zone.

However, this reaction also has a negative effect, since the glass surface already begins to corrode during the cooling phase after forming (see Chapter 3.2).

- The glass surface reacts with atmospheric humidity at temperatures from 600°C to room temperature. Hydroxyl (OH⁻) groups, which are highly reactive and an extremely important element of the coating process, are formed both within and on the glass surface (see Figure 3.1.2).

Figure 3.1.2
Diagram of the flat glass surface
with terminal hydroxyl groups



Due to the reactions described both within and on the flat glass surface, the surface now possesses different properties from the glass body. The de-alkalisation due to sodium evaporation alters almost all the physical and chemical properties of the surface of the glass. Chapter 3.2.1 deals with this in more detail. Due to their high reactivity, the hydroxyl groups on the surface ensure strong adhesion of the coated layers to the surface in many cases. However, they also have the disadvantage that they adsorb humidity so that the glass surface is always covered with a thin film of water which, of course, tends to have a negative effect on the coating process. The hydroxyl groups on the glass surface are the reason for glass being hydrophilic (see also Chapter 5.5.1).

Figure 3.1.3 shows the glass surface covered in an adsorbed water film as well as the bonding energy of the latter depending on the film thickness.

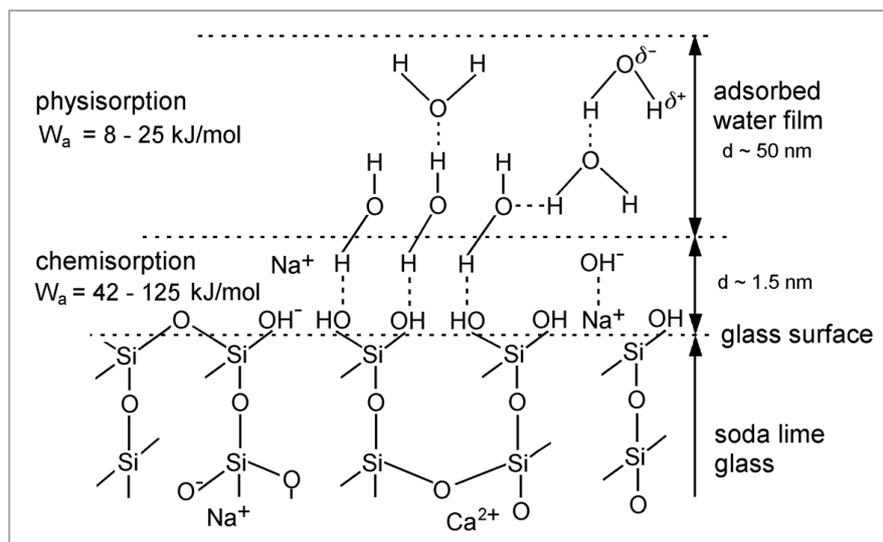


Figure 3.1.3 Diagram of a glass surface covered with an adsorbed water film

(source: PULKER)

It can be seen that the upper part of the water film is only loosely linked by residual valences (VAN DER WAALS forces). The adsorption energy W_a , which is a measure for the bonding energy (see explanation in Chapter 5.5.1), amounts only to 8-25 kJ/mol. The rather loose

bonding of such films to surfaces is called physisorption. The thickness of this part of the water film depends on temperature and air humidity; it can reach a maximum of about 50 nm. However, the lower part of the water film is much more closely linked, its adsorption energy amounts to 42-125 kJ/mol. This kind of bonding is called chemisorption (see also Chapter 5.5.1). It is based on an exchange of electrons between atoms of the glass surface and the adjacent water film. The thickness of this part of the water film is only about 1.5 nm. While the upper part can be removed fairly easily, temperatures of over 400°C or another sufficiently high level of incident energy (e.g. due to ion or electron bombardment) is needed to remove the lower part, i.e. removing it by splitting up the chemisorptive bonds is a fairly arduous process. If the coating process is disturbed by the water film, it is more advisable to deposit an adherence-enhancing layer which integrates the water film, rather than trying to remove it. Bismuth oxide, for example, has excellent adhesive properties both to the glass surface and to further layers.

As mentioned in Chapter 1.4.2, the flat glass surface is weakened by a large number of micro-flaws which appear immediately after the forming process and can therefore be counted as natural properties of the flat glass surface. The number and size of these micro-flaws depends on the glass composition and the manipulation of panes, as well as on the extent of corrosion after forming.

Because the flat glass used for coating purposes today is predominantly float glass, it is important to explain some of its special properties.

The forming process on a tin bath (see Chapter 1.2) results in the glass ribbon having two different surfaces. During forming, the upper surface is in contact with the reducing forming-gas atmosphere which consists of 95 % nitrogen (N₂) and 5 % hydrogen (H₂), while the lower surface rests on the molten tin. The upper surface is known as the 'atmospheric surface' and the lower one is the 'bath surface'.

The differences between the two faces become apparent with certain surface properties which are important for the coating process. Due to the contact with the tin bath, the sodium content of the bath surface is lower than that of the atmospheric surface. Through this contact, tin ions (Sn²⁺) diffuse into the bath surface. It has been found that, as a result of this, its refractive index, scratch resistance and resistance to several chemicals are higher than on the atmospheric surface. The water resistance of the bath surface, however, is weaker because the tin ions which have diffused into the surface and are not evenly distributed over the pane surface react with water. Thus when the surface is heavily attacked by water, localised signs of erosion can be found, i.e. corrosion takes place locally there (see Chapter 3.2). In addition, the reactivity of the bath surface and the atmospheric surface differs. The bath surface has a more reducing effect for reactions on the surface because of its Sn²⁺ content. Furthermore, the bath surface wettability declines substantially with time, which can be a significant disadvantage, e.g. if the glass is intended to be used as a slide for microscopy. This disadvantage of the bath surface can be compensated for by depositing a layer of silicon oxide (SiO_x) immediately after the float glass has been cooled in the production process. This ensures a long-term wettability of the bath surface (see Chapter 5.5.2, Part II).

Another difference concerns surface roughness. Figure 3.1.4 shows atomic force microscope (AFM) images of both the bath and the atmospheric surfaces. Measurements based on AFM imaging have determined that the atmospheric surface has a roughness of 4 - 10 nm,

whereas on the bath surface it is only 1.2 - 2 nm. However, the two surfaces cannot be distinguished by the naked eye, although under ultraviolet radiation they behave differently. The tin ions in the bath surface are excited by ultraviolet light so that they fluoresce bluish white, which can be observed clearly in a darkened room. This method is often used to determine the surfaces of float glass.

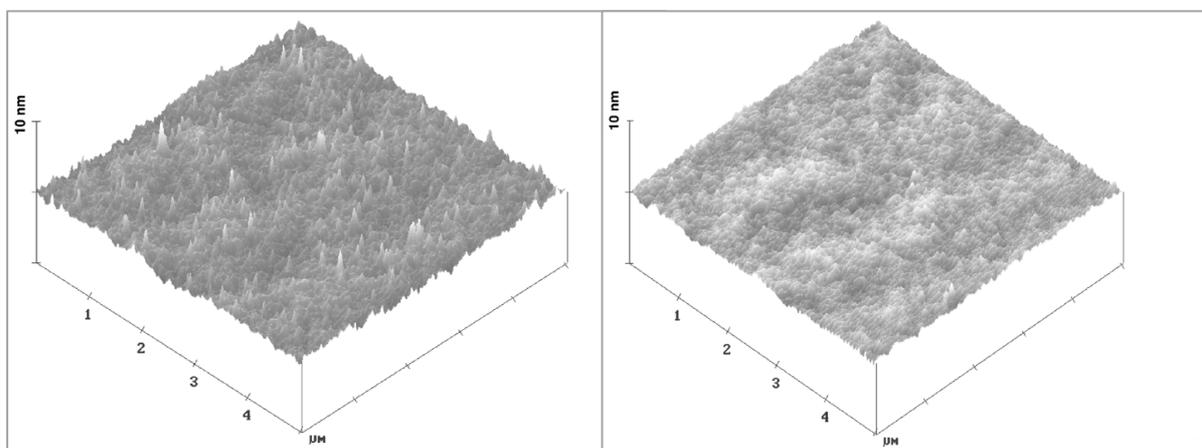


Figure 3.1.4 AFM images of a) the atmospheric surface and b) the bath surface of a float glass pane

(Source: E. RÄDLEIN, Technische Universität Ilmenau, Germany)

The glass surface (bath or atmospheric) has no effect on the properties of most of the commonly applied functional thin film layers. However, there may be certain coatings where the glass surface does play a role. When developing new coatings on float glass panes, it is always important to check before whether the properties of the coating are affected by the different glass surfaces.

3.2 Corrosion of the glass surface

3.2.1 The origin of corrosion and its effects on coatings

The term 'corrosion' originates from the metallurgical industry where the term denotes the attack on a metal surface by an adjacent substance. The generation of rust (ferrous hydroxide and iron oxides) on steel surfaces due to contact with the atmosphere and humidity serves as a classic example of corrosion. Similarly, glass corrosion denotes a glass surface being attacked by adjacent substances. In the case of glass panes which are to be coated, significant corrosion can occur due to humidity or even dewing during storage or transportation or due to cleaning liquids, if the panes are cleaned prior to the coating process.

As described in Chapter 3.1, the chemical reaction underlying the corrosion process is dealkalisation, i.e. alkali (Na^+) and hydroxide (OH^-) ions are leached out of the glass surface. A permanent thin film of water on the glass surface causes these ions to form fairly concentrated sodium hydroxide (NaOH) with the course of time. A self-accelerating alkaline decomposition of the glass structure then follows, which results in the destruction of the surface up to a depth of several micrometres. This results in a matt surface like a grinding. If the water film is renewed continuously, as is the case with window panes which are exposed

to rain, the glass surface is no less de-alkalised, but the self-accelerating decomposition does not take place. On the contrary, this layer of corrosion which arises preserves, i.e. 'improves' the surface. The corrosion film on the surface of flat glass is a porous SiO_x layer which is low in sodium, i.e. a layer of silica gel, which can extend several micrometres deep into the glass surface. But during the storage, transportation or cleaning of the pane prior to the coating process, the silica gel layer is liable to accumulate all kinds of impurities, causing a negative impact on additional coatings.

It has already been seen in Chapter 3.1 that the flat glass surface starts to corrode immediately after the forming process because of chemical reactions with the surrounding atmosphere. De-alkalisation using sulphur dioxide (SO_2), a deliberate process which is intended to protect and lubricate the glass pane for transportation on roller conveyors, has been pointed out to be an important reaction. This chemical reaction, however, takes place on the glass surface, i.e. it does not interfere essentially with the glass body itself. But the de-alkalisation process may continue due to air humidity and/ or dew and thus extend into the glass body.

Figure 3.2.1.1
Schematic diagram of the corrosion of soda lime glass
(source: HENCH and SANDERS)

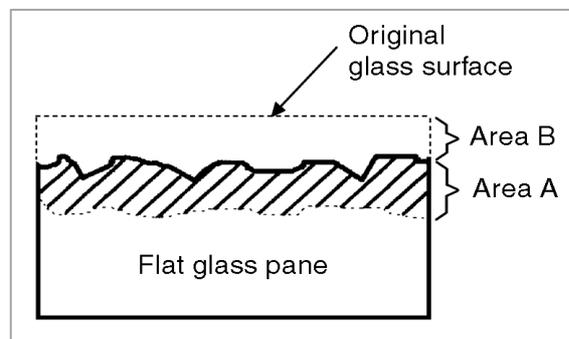


Figure 3.2.1.1 shows the generation of a layer of glass corrosion, through the example of a soda lime glass pane. There are two different areas which are typical for soda lime glass corrosion processes:

- 1) Area A shows a porous silica gel corrosion layer, which originates when sodium leaches off the glass surface. The corrosion layer has a higher SiO_2 content than the glass body, as well as some remaining soda and other lattice-changing substances such as calcium ions (Ca^{2+}). Moreover, crystalline precipitates of calcium carbonate (CaCO_3), for example, can be observed. These are produced by reactions with certain components of the air.
- 2) Area B shows the erosion of the entire substance of the glass, which occurs simultaneously with the leaching process.

The thickness of the corrosion layer depends on the one hand on the composition of the glass and on the other on the physical properties of the surface, such as the roughness, mechanical tension, damage (such as cracks and abrasions) and pre-treatment. In addition, it is influenced by how the water film is generated (wetting by water or vapour condensation), by the reaction temperature and reaction time and by the number of wetting/ drying alternations, i.e. how often the dew point is exceeded and fallen below.

If flat glass is stored at low humidity and constant low temperatures, i.e. without getting wet with dew, the corrosion proceeds very slowly because the leached sodium hydroxide (NaOH) reacts with CO_2 in the air to become sodium carbonate (Na_2CO_3) on the glass surface. This delays the corrosion process considerably and so the flat glass surface is in effect preserved.

If stored at high humidity and fluctuating temperatures, so that dew occurs constantly, a distinct layer of corrosion quickly appears. Often the water attack is not evenly distributed over a large pane and so the corrosion layer is also unevenly distributed.

The corrosion layer possesses properties different from the glass body. For instance, the refractive index (see above) and the thermal expansion are lower than in the glass body. This may have a positive effect on some glass refinement procedures. For coating applications, however, corrosion layers are generally negative because of the way they change the chemical and physical properties and because of the uneven distribution of the corrosion across the glass surface. Technical data of mirror (reflection-enhancing) and anti-reflection layers can be incorrect because of the changes in the refractive index. This is manifested as colour irregularities or as “fogging”. It is also known that layers, particularly thin layers, grow differently on top of a corrosion layer because of the change in surface energy. Severe corrosion layers may lead to instances of visible interference, since the refractive index of the glass body and the corrosion layer are different. If the corrosion is unevenly distributed over the surface, it causes iridescence on the pane (see also Chapter 5.1.2.1). Such a pane is under no circumstances suitable for coating purposes.

Furthermore, the corrosion layer may affect the ageing behaviour of the coatings. Because of the porosity of the corrosion layer, impurities easily stick to its surface and penetrate into it. These impurities may cause chemical reactions with the layer, resulting in the premature ageing of the layers deposited on top. This can lead to an alteration of the properties of coatings and may destroy their function.

To summarise, corrosion layers on flat glass surfaces cannot be avoided and these layers usually have a harmful effect. Therefore it is important to minimise the surface corrosion of flat glass intended for coating purposes.

3.2.2 Methods to avoid and remove corrosion layers

There are a number of ways to limit the extent of corrosion of flat glass surfaces:

- 1) The use only of newly-manufactured flat glass for coating purposes, i.e. the coating process should follow the manufacturing process immediately. However, even if the panes are coated in the glassworks, it is not always feasible for the coating process to be carried out straight away.
- 2) If newly-manufactured flat glass is not available, glass which has been stored at constant temperatures and at controlled humidity should be used. This would require storage in air-conditioned rooms and, in effect, is rarely possible at glassworks locations, due to the large production capacity of float glass plants nowadays. Flat glass which has been stored under fluctuating climatic conditions for a long time (e.g. if stored near shed doors) should particularly be avoided for coating purposes.
- 3) Another option is to seal the pane stacks at their edge so that they are air-tight and humidity cannot enter them. This technique is customarily applied today to stacks of panes which are already coated, but it is not yet common practice for the raw material, i.e. uncoated panes.
- 4) Flat glass can also be preserved chemically by applying suitable acidic buffer substances onto the pane surface, which prevents the leaching process. Chemical

buffers which have been tested and proved effectively in practice are sulphurous acid, zinc amine chloride, acetic acid, adipic acid, lactic acid and partly also sulphuric acid. Recently, good experiences have also been made with boron oxide. Today acidified polymethyl methacrylate (PMMA) beads are used almost exclusively, acidified paper sheets are only rarely used for reasons of cost. The vapour pressure of the acids employed for preservation purposes should ensure that the glass surface is protected uniformly throughout the time of in-house storage and transportation of panes. Lactic acid has certain advantages here. However, this acidification has not yet become standard in industrial practice. Adipic acid most commonly used for the protection of flat glass nowadays, however, has the disadvantage that it produces insoluble sodium adipinate if exposed to water, e.g. by dew, for a longer period, which results in faulty coatings.

- 5) Corrosion layers can be removed chemically and mechanically by etching or polishing the pane surface immediately before the coating process. Both cases are instances of subtractive refinement processes (see Chapter 2.2).

Chemical removal can be performed by etching, e.g. through the application of 0.5 % hydrofluoric acid (HF) for 15 - 60 seconds. The process can only be employed if the corrosion has not progressed too far, otherwise the surface would be roughened too much and so become matt, which is not usually the desired outcome. In addition, it should be considered that the use of hydrofluoric acid (which is very aggressive) and its subsequent neutralisation is hazardous to the environment. In practice, the etching of flat glass panes in order to remove corrosion layers is not utilised as a means of preparing the large area panes for coating. However, the process is used to a limited extent when smaller flat glass panes are etched with weaker chemicals in order to remove corrosion, usually in combination with ultrasonic cleaning processes (see Chapter 3.4).

The removal of the corrosion layer by polishing is generally classified as a mechanical process. In reality, however, polishing is a rather complex friction-wear procedure in combination with chemical reactions. It is carried out using appropriate polishing agents, such as a suspension of cerium oxide (CeO_2), ferric oxide (Fe_2O_3) and other oxides, as well as substances containing polishing agents, e.g. made from polyurethane, araldite, felt, pitches and waxes. However, polishing processes are often too expensive for treating large surface areas of glass. Their use is therefore restricted to smaller panes which require top-quality surface conditions, for example panes intended for use as laser mirrors or disk carrier plates. A mild polishing process is also successfully employed prior to the coating of mirrors (see Chapter 4.3.1.2). It should be noted that polished flat glass panes are more prone to corrosion, because the natural protective Na_2SO_4 layer, which is generated during the manufacturing process, is destroyed through polishing. The panes must therefore be coated as soon as possible after polishing. This also holds true for conventionally cleaned (i.e. washed) panes.

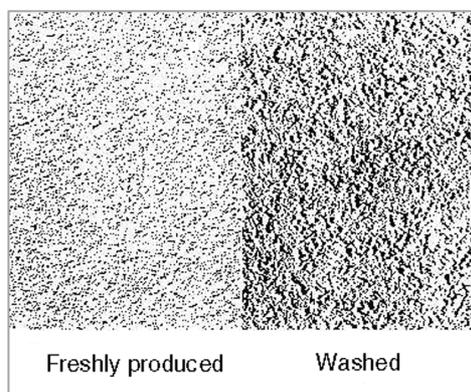
Polished or washed panes should be coated immediately.

A tried and tested procedure of getting round the problems of coating glass which is attacked by corrosion is to follow the rule: '**Work with the corrosion, not against it**'. This is based on the assumption that it is easier to choose an appropriate coating process, coating material and layer structure, so that a fully functional coating can be deposited uniformly and

reproducibly onto the corroded flat glass surface, than it is to try to remove the corrosion layer. The careful selection of a suitable blocking and adhesive layer, which is deposited immediately onto the flat glass surface, is of primary importance here. Bismuth oxide (BiO_x), for instance, is a substance which has proved to compensate for the negative properties of corrosion layers extraordinarily well. It must be pointed out though, that this ingenious process is not appropriate for heavily-corroded flat glass surfaces, e.g. with visible iridescence.

To minimise corrosion, attention must also be paid to the pane cleaning process prior to the coating process. In the final cleaning stage, at least, highly-purified, i.e. residue-free, water which is chemically very aggressive is used. Figure 3.2.2.1 shows how the water used for the cleaning process can attack the flat glass surface. It can be seen that during the washing process the flat glass surface is roughened due to leaching and chemical attacks. It is important to emphasise that the glass surface should not be in contact with highly-purified water for too long, especially if the water is hot.

Figure 3.2.2.1
Flat glass surface before
and after washing
(source: HOLLER)



3.2.3 Checking the glass surface for corrosion

As glass corrosion has such a serious effect on coatings, it is advisable to check the flat glass panes intended for coating thoroughly for corrosion before the coating process and to classify them accordingly. This was often problematic in the past, but surface analysis methods are now sufficiently well-developed so that it is feasible to check at least samples of flat glass surfaces in the laboratory.

Formerly, a silver layer was deposited chemically onto the carefully cleaned flat glass pane using a wet process, similar to the silver mirror coating process explained in Chapter 4.3.1.2. In this way the glass surface quality could be evaluated, because it was known that layers of silver deposited immediately onto the glass surface are very sensitive to glass corrosion and other surface impurities. As long as no irregularities, for instance fogging, could be detected in a visual inspection of the silver mirror after the test coating, the batch of panes was labelled as 'coating quality'. This quality class is adequate for the large majority of flat glass coatings carried out today. Nevertheless, with this evaluation method no conclusions can be drawn about the thickness and composition of corrosion layers.

HENCH and SANDERS have described the detection of corrosion layers by measuring the spectral infrared reflection at a wavelength λ of around $10\ \mu\text{m}$. This method of measurement is based on the fact that layers of corrosion have a higher SiO_2 content than the glass body

and that SiO_2 has characteristic vibrations at a wavelength of around $10 \mu\text{m}$. Figure 3.2.3.1 describes the functional principle of this method of measurement.

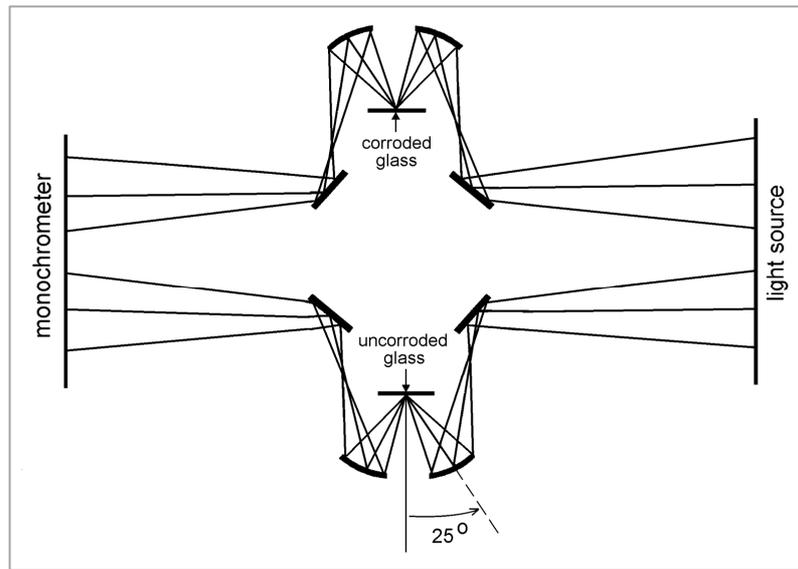


Figure 3.2.3.1 Principle of the spectral-photometric double beam method of measurement as used for the evaluation of glass corrosion layers
(source: HENCH and SANDERS)

The measurement is made by means of a dual beam photometer at an angle of incidence of 25° . One beam targets the corroded glass sample, while the other beam targets a virgin reference sample. In this way the corrosion layer can be measured very precisely. The most precise information for soda lime glass is achieved when measuring the reflection at a wave number of 950 cm^{-1} . Figure 3.2.3.2 shows the spectral curves of corroded and virgin soda lime glass.

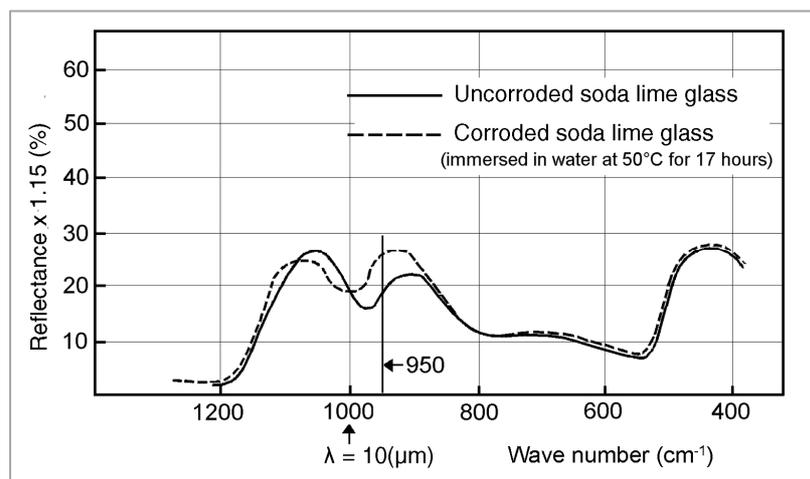


Figure 3.2.3.2 Infrared reflectance curves of corroded and virgin soda lime glass
(source: HENCH and SANDERS)

It is easy to imagine that this method of measurement would be suitable for the evaluation of flat glass on the production line prior to the coating stage.

In recent decades, a flood of surface and layer analysis methods have been developed which are, in part, suitable for detecting glass corrosion. All the most important methods for the evaluation of glass surfaces are based on the following physical principles:

- Atomic excitation on and in the glass surface by means of electrons and the detection of characteristic recombination radiation of those atoms
- Surface erosion by means of ions and the mass spectrometric detection of eroded atoms
- Grazing incidence of X-rays onto the surface and the measurement of reflection, absorption and fluorescence
- Scanning the surface by means of a scanning tunnel microscope or an atomic force microscope

Methods of measurement utilising the first principle of surface atom excitement are based on photoelectron spectroscopy (PES) or on Auger electron spectroscopy (AES), i.e. the light signals or electrons emitted by the excited surface atoms are detected and evaluated. The glass surface is not destroyed by these measurement methods.

In the second case, the surface is partly ablated and thus destroyed in order to analyse the released atoms. An analytical process based on secondary neutral particle mass spectroscopy (SNMS) is especially suitable for glass surface evaluation purposes. For further reading on the mentioned methods of analysis, the works of authors such as BACH and OECHSNER to be found in the References section of this book are recommended.

With surface evaluation methods utilising the principle of X-rays with grazing incidence, the glass surface also remains undamaged. Using this analytical approach, a great deal of information on the interfaces and layers can be gathered. It is possible to investigate the chemical composition, thickness, density and roughness of any kind of layer on flat glass simultaneously. It is very well suited to the investigation of corrosion layers on flat glass. For further reading on this method of analysis, the works of authors such as HÜPPAUF, LENGELER, ANDERSON and BANGE to be found in the References section are recommended.

Glass surfaces (and, in the same way, layers of corrosion) can be analysed by means of surface scanning methods, also called scanning sensor methods. Scanning tunnel microscopy (STM) and atomic force microscopy (AFM) are employed for this. For further reading on this method of analysis, the reader is recommended to consult the work of authors such as RÄDLEIN to be found in the References section.

All the described methods of analysis require expensive measuring equipment, as well as laborious sample preparation. Therefore, they are mainly used today in the laboratory.

3.3 Impurities on flat glass surfaces

Impurities consist of foreign matter which contaminates the surface of the glass. Such substances adhere strongly or not so strongly to the flat glass surface and can impair the coating process and the coatings themselves. Impurities may originate during glass production or during subsequent processing stages. The impurities which arise during production are:

-
- Gases and vapours adsorbed from the surrounding air during the production process, e.g. oxygen (O₂), nitrogen (N₂), carbon dioxide (CO₂), sulphur dioxide (SO₂), hydrochloric acid (HCl), water (H₂O) and so forth
 - Dust particles from the surrounding air
 - Sodium sulphate (Na₂SO₄) (see Chapter 3.1), which is generated on the glass surface as the cooling zone is fed with SO₂. Sodium sulphate acts as a lubricant for the transportation of panes on roller conveyors and so protects the glass from scratches and abrasions. It is water-soluble.
 - Materials (or remnant particles of them) used to protect panes from scratches and abrasions during in-house or long-haul transportation of glass. Today, the most commonly used materials are PMMA beads or paper sheets (see Section 3.2.2).

Impurities originating in the glass manufacturing process are unavoidable. Today their removal from the glass surface is no longer problematic, with the exception of water films and remnant particles of the material used to protect panes during transportation.

The main impurities which arise during subsequent processes come from

- Cutting oil, if the panes are cut to size
- Dirt depositions from intermediate storage prior to the coating stage
- Contamination originating during handling procedures, such as finger prints or marks left by vacuum lifting equipment
- Residues of cleaning agents from the washing stage prior to the coating process

Impurities, especially those generated during the processing and handling stages, can be chemisorbed by the corrosion layer, i.e. they may stick so fast that they cannot be removed by the usual cleaning methods. Marks left by vacuum lifting equipment used to transport the panes may be a particular problem, because the form release agent used when making the rubber sucker heads may react chemically with the corrosion layer when it contacts the glass surface. The compounds resulting from this reaction create circular marks which cannot be removed through ordinary cleaning methods. The surface energy (see Chapter 5.5.1) and optical properties of these marks differ from those of untouched glass surfaces. The different surface energy leads to different growing behaviour of coatings which, in turn, may cause coatings to build up unevenly with different optical properties. This can also result in disruptive, uneven humidity condensation (dew wetting), if the pane is used for window glazing and the surface in question faces outwards. Similar surface energy problems occur with cutting oil residues, finger prints and remains of sticky labels etc.

Impurities may cause the following negative effects on coating properties:

- They act, in effect, as form release agents between glass surface and functional layer and so prevent sufficient adherence between the two.
- They influence the properties of the coating. Like corrosion layers, they can, for instance, alter the optical (see above) or electrical properties.
- The resistance to ageing can be influenced due to chemical reactions between coating and impurities.

It should be noted that the flat glass surface is chemically very sensitive. Impurities can be actually engraved into the glass through chemical reactions. Since impurities generated during processing stages are avoidable, efforts should be made to prevent them from occurring.

When processing flat glass panes prior to coating, attention should be paid to the following handling rules:

- 1) Flat glass panes should be handled with extreme care and only if necessary.
- 2) Suitable gloves should be worn when handling flat glass panes.
- 3) The sucker heads of lifting equipment should be covered with a thin piece of soft fabric, in order to avoid chemical reactions between the rubber and the glass surface.
- 4) The cutting oils used for glass cutting should be easily and completely removable by evaporation. Suitable oils are available today from specialist companies. Petroleum, which was used formerly as a cutting aid, causes residues on the glass surface which usually disrupt the coating.
- 5) Cut-to-size panes should be properly stacked when stored before coating.

Remember: impurities which are avoided do not have to be removed!

Despite the greatest care while processing or handling panes, it is natural that minor impurities cannot be avoided completely during today's industrial-scale processes which involve industrially-processed materials like flat glass. Therefore, flat glass has to be cleaned before it can be coated, at least when the coating process is independent of the flat glass production process, i.e. 'off-line', in contrast to coating 'on-line' with the flat glass production process. As the flat glass surface is chemically very sensitive, cleaning processes are particularly critical when sensitive layers are to be deposited. As mentioned in Chapter 3.2.2, where the avoidance of glass corrosion is discussed in detail, and in view of the particles which unavoidably remain after the cleaning process, it is advisable to deposit a suitable blocking and adhesive layer onto the glass surface prior to the functional coating, to cover minor spots of corrosion and impurities. It is a great advantage of coating processes on-line with the flat glass production that cleaning procedures can be bypassed completely.

3.4 Preparation of the flat glass surface for coating

3.4.1 Purity requirements for flat glass surfaces which are to be coated

According to the description in the previous chapter, the glass surface must be clean for coating. This will be the case *a priori* for on-line coating processes, but care must be given that it is also achieved for off-line coatings. Generally it must be said that, especially for large panes, absolute purity is impossible to achieve. Therefore, it is important to determine the necessary level of cleanness required for the coating in question. This level of cleanness has to be sufficiently high so that the deposition of a uniform, reproducible coating, which is suitably resistant to ageing, can take place across the entire pane surface. This means that the level of cleanness has to be matched to the

- Requirements of the coating

- Coating process
- Coating material
- Quality of the available flat glass (as regards the surface to be coated)

This is a question of quality and costs. The interdependencies shown here can be quite complex, particularly when special coatings are required. For this reason, the best possible cleaning process forms a substantial part of coating expertise. The quality requirements for the purity and condition of flat glass surfaces intended for coating can only be fulfilled if all the factors mentioned above are taken into consideration. The only statement about quality which always holds true is that the level of cleanness must be uniform over the entire pane surface, which is often difficult to achieve for large panes.

Because each individual coating requires different surface qualities, only the functional principles of cleaning methods used today will be explained here.

3.4.2 Cleaning processes for flat glass panes intended for coating

Generally, a distinction is made between wet and dry cleaning processes. Dry cleaning processes utilise low-pressure plasma technologies, where the surface to be cleaned is bombarded with ionised, high-energy gas ions from a plasma under vacuum conditions, comparable to the sputtering technologies explained in Chapter 4.2.1. The surface is cleaned because the bombarding gas ions cause the surface contaminants to evaporate. This dry cleaning method is environmentally-friendly, but it only has limited uses, because it does not remove all impurities. It is therefore not suitable for the total cleaning of large panes. However, it is often employed to remove films of water or oil from glass surfaces and to form coating-promoting “seeding layers” in a preliminary stage prior to vacuum coating processes. This pre-treatment with a low-pressure plasma is called ‘glowing’. However, there is some controversy as to the effectiveness of the glowing process with large-area panes.

In order to prepare large-area glass panes for coating, today only wet cleaning technologies are used. Wet cleaning technologies comprise three stages:

- 1) Loosening of the impurity on the glass surface
- 2) Removal of the separated impurity
- 3) Drying of the cleaned glass surface

The second step often used to be neglected. This led to the effect shown in Figure 3.4.2.1.

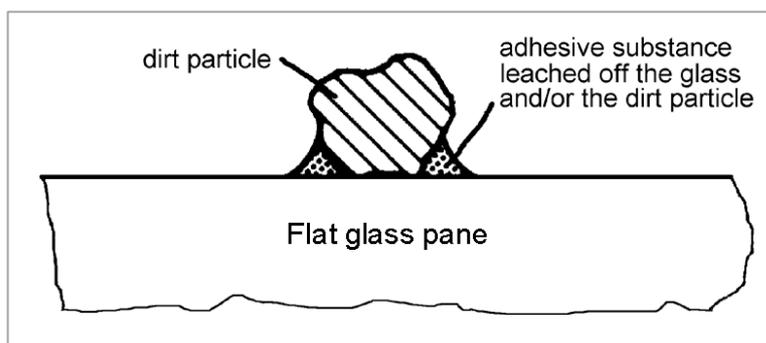


Figure 3.4.2.1 Burnt-in dirt on a glass surface

Loose impurities which are not properly removed can actually 'burn into' the glass surface during the subsequent drying stage. These burnt-in impurities are almost impossible to remove with a repetition of the cleaning process, so that a pane with burnt-in impurities must usually be discarded. Loose impurities can only be removed by extensive rinsing with highly-purified water. For cost reasons, many companies often used to be too sparing with water.

Both mechanical and chemical processes can be used to loosen or separate the impurities from the glass surface. Mechanical processes include

- Ultrasonic (US) cleaning
- Brush cleaning
- High-pressure jet cleaning in some cases

Chemical cleaning can be done with

- Water for pre-cleaning
- Diluted alkaline or acidic solutions
- Various tensides and detergents
- Highly-purified water for the main cleaning process and rinsing

Chemical cleaning processes have the additional advantage that the flat glass surface can simultaneously be activated to take a coating. The water for the main cleaning process and subsequent rinsing is prepared with special water purification plants (see below).

The three mechanical wet cleaning processes will be described in the following paragraphs. Because of their importance for wet cleaning processes, the supply of highly-purified water and the applied drying processes will be discussed separately.

Ultrasonic (US) cleaning

The principle of the US cleaning technology is to immerse the object to be cleaned in a vibrating liquid. So that there is no interference with radio transmissions, the permitted frequencies of 25 Hz and 40 kHz are used as vibration frequencies. The impurities are loosened from the surface by the cavitational power of the vibrating liquid. Figure 3.4.2.2 shows a typical ultrasonic cleaning plant for flat glass panes.

The plant consists of a sequence of several cleaning tanks. The panes stand vertically in a holder and are immersed in the tanks. Tanks 1 and 3 are equipped with a vibrator (5). Tank 1 contains an alkaline medium, which is intended to have an effect on the glass corrosion while cleaning the glass. Tank 3 contains an acidic solution, which is intended to achieve both acidic polishing and surface activation, i.e. an adherence-enhancing effect. Acidic liquids can break Si-O-Si bonds on the glass surface (see Figure 3.1.2) resulting in very reactive hydroxyl groups (here Si-OH). The particular liquids used in Tanks 1 and 3 and the temperature and duration of the process depend on the application concerned. As the ultrasonic vibration causes static waves in the tanks, the panes are moved about in the tanks during the cleaning process, in order to ensure the complete cleaning of the entire surface. In Tank 2 the panes are rinsed with ordinary or highly-purified water, and Tanks 4a and 4b ensure an intensive, two-stage, final cascade rinse of the cleaned surfaces with highly-purified water.

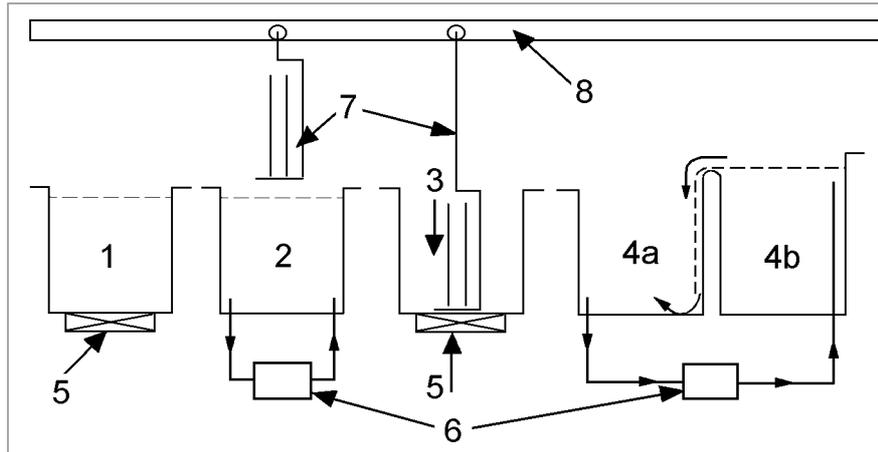


Figure 3.4.2.2 Diagram of a US cleaning plant for flat glass

- 1: US cleaning in alkaline solution
- 2: Rinsing with purified water
- 3: US cleaning in acidic solution
- 4a/b: Cascade rinsing with highly-purified water
- 5: US transducer
- 6: Water purification plant
- 7: Support for flat glass panes
- 8: Transport rail

Because ultrasonic cleaning is based on immersion techniques, only pane sizes up to about 1 m² can be cleaned economically. Otherwise, the pane transportation and the amount of space required would make such plants too expensive.

High-pressure jet cleaning

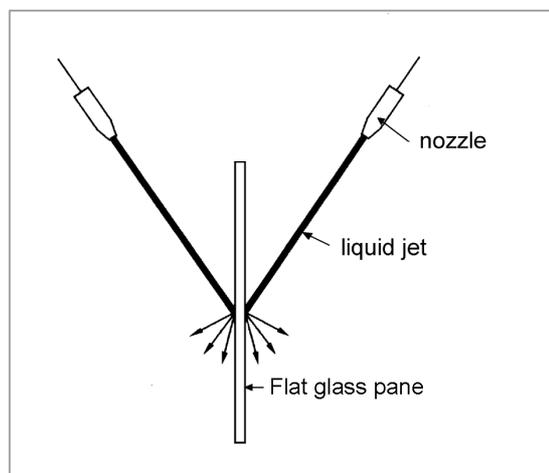


Figure 3.4.2.3
Diagram of the high-pressure jet cleaning method

Figure 3.4.2.3 shows a diagram of the high-pressure jet cleaning method. With this method, flat glass panes are sprayed on both surfaces with a cleaning liquid under high pressure. For the cleaning of large panes, the supply tubes are fitted with a number of nozzles which oscillate at right-angles to the direction of conveyance of the panes, so that the entire surface is treated by the cleaning jets. Like the brush cleaning plants (see Figure 3.4.2.4), high-pressure jet cleaning plants consist of a sequence of several cleaning zones. Each cleaning zone contains pairs of nozzles. The panes can be moved through the plant either by conventional rollers or by suspending them from a holding device, only touching their

surfaces at the upper end. The latter method is frequently used when cleaning flat glass panes which are intended to be coated with highly surface-sensitive layers e.g. utilising the sol-gel dipping technique (see Chapter 4.3.3). Because there are several cleaning zones in sequence, it is possible to use various cleaning liquids and highly-purified water, according to the needs of the actual application.

High-pressure jet cleaning plants are used relatively seldom. However, with such arrangements of jets all commonly available pane sizes can be cleaned in principle.

Brush cleaning

The principle of brush cleaning is to separate dirt from the flat glass surface mechanically by brushing it and removing the dirt particles with water or other cleaning liquids sprayed onto the pane through nozzles. Both drum and disc type brushes are used for flat glass cleaning, but pairs of drum brushes being the most commonly-used arrangement. The two brushes rotate against one another and the pane is moved between them. The drums are a little longer than the maximum pane width. Their bristles are between 0.25 mm and 0.95 mm in diameter and the brushes rotate at about 680 revolutions per minute. Drum brush cleaning plants can be designed either for horizontal or for almost vertical pane conveyance (minimum deviation from the vertical: 6°), depending on the coating process to follow. Figure 3.4.2.4 shows a diagram of a vertical drum brush cleaning plant.

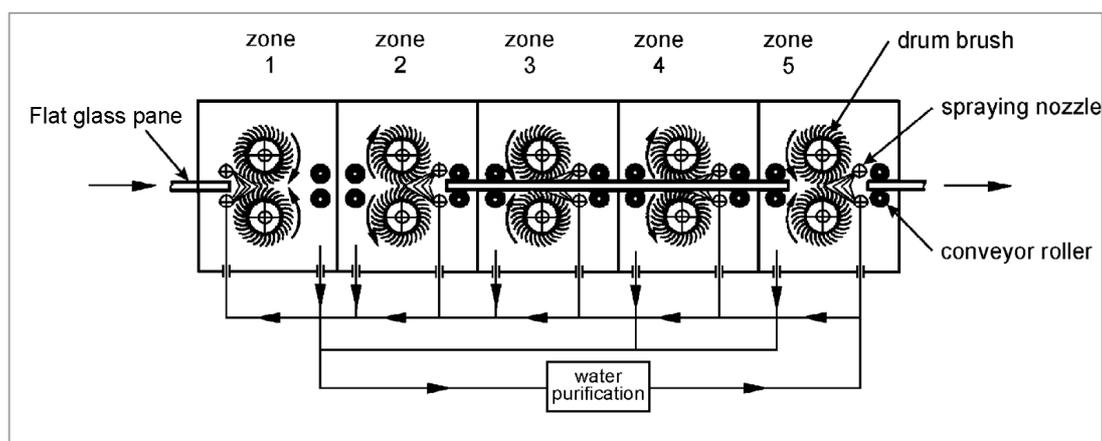


Figure 3.4.2.4 Diagram of a vertical drum brush cleaning plant for flat glass cleaning (top view)

The plant consists of a sequence of cleaning zones. Each cleaning zone is equipped with a pair of drum brushes and spraying nozzles along two tubes on both sides of the pane. Again, the spraying width is a little larger than the maximum pane width. The panes are transported by conveyor rollers; arranged vertically in pairs for vertical conveyance and horizontally in rows for horizontal conveyance. The conveyance rollers are preferably covered with EPDM rubber. The number of cleaning zones depends on the required level of cleanness and the cleaning speed. In the plant shown in Figure 3.4.2.4, each cleaning zone has its own separate washing liquid supply. However, there are also plants which use the washing liquid in cascades, i.e. the fresh liquid is fed into the last (the cleanest) zone and then re-used in the form of a cascade in the other zones until it reaches the first (the dirtiest) zone. For rinsing, only highly-purified water is ever used. Recently, chemical cleaning liquids have begun to be used again instead of water, in some of the cleaning zones (as was the case

several decades ago). The aim is not only to clean the panes but also to remove corrosion layers and other contamination at the same time. Of course, this adds considerable effort and expense for admitting and disposing of the cleaning agents.

Disc brushes are preferred if the panes are to be cleaned on one surface only, i.e. the surface to be coated, in horizontal plants. In cleaning plants for large panes, a number of disc brushes, fixed side-by-side on a bridge, oscillate over the panes at right-angles to the direction of conveyance of the panes. Disc brushes are employed particularly when a mechanical polishing effect is intended in addition to the cleaning. They are conventionally installed in cleaning plants for silver coating in order to produce mirrors (see Figure 4.3.1.2.1).

Drum brush cleaning plants are by far the most frequently used type of cleaning plants for large float glass panes. They are capable of cleaning panes of a size from 30 cm x 30 cm up to the jumbo size of 3.21 m x 6.00 m. In these plants, the minimum possible pane size depends on the distance of the conveyor rollers from each other. Drum brush cleaning plants can handle panes from 3 to 13 mm thick; the optimum distance of the drum brush pairs to the flat glass surfaces can be adjusted automatically.

One of the problems of brush cleaning plants is that there are often a number of 'dead' corners, where dirt particles accumulate during the cleaning process. As these dirt particles make the cleaning process difficult or even impossible, it is important that cleaning plant manufacturers try to eliminate such dead corners. In addition, all cleaning plants require regular maintenance to ensure the desired cleaning effect.

Water purification systems

Water purification systems supply process water for the cleaning stage. Ordinary municipal water is not pure enough for the main cleaning and for the rinsing stage – the level of foreign chemical or biological substances in dissolved or solid form, i.e. particles or germs, is too high.

The purity level of water is determined by a number of factors. One method used to check the level of dissolved substances is electric conductivity, measured in Siemens (S). It must be noted though that different substances contribute to the conductivity in various ways, so that the composition of the impurities forms a major criterion, too. The size and number of particles and the number of germs per litre are further criteria referred to when evaluating water purity. Table 3.4.2.1 shows the quality requirements for the cleaning water which is used for cleaning flat glass panes prior to coating. It can be seen that coatings for electronic applications such as LCDs (see Chapter 6.1.1, Part II) require much purer cleaning water than coatings on glass for construction.

The purity which is necessary for the actual application can be provided by water purification systems, which reduce the foreign matter content to the required degree. Figure 3.4.2.5 shows the flowchart of a modern water purification plant for the supply of highly-purified water for cleaning panes which are processed to flat displays.

Such water purification systems mainly consist of several purification stages in sequence: filters, ion exchangers or reverse osmosis units, and UV radiators through which the water is pumped before it is collected in a storage tank. The high-performance system shown in

	for coating of	
	constructional glass, silver mirrors	conductive glass, e.g. for LCDs
electric conductivity [$\mu\text{S}/\text{cm}$]	< 1	0.0555
hardness, measured as CaCO_3 content [ppm]	0	0
silicic acid [ppb]	< 100	< 3
total organic matter [ppb]	< 1,000	< 10
number of particles > 0.5 μm [per l]	< 1,000	< 100
number of particles > 0.2 μm [per l]	< 10,000	< 1,000
number of germs [per l]	< 1,000	< 10

Table 3.4.2.1 Quality specifications for water used to clean large-area flat glass panes before coating

(source: Falk GmbH Westerburg)

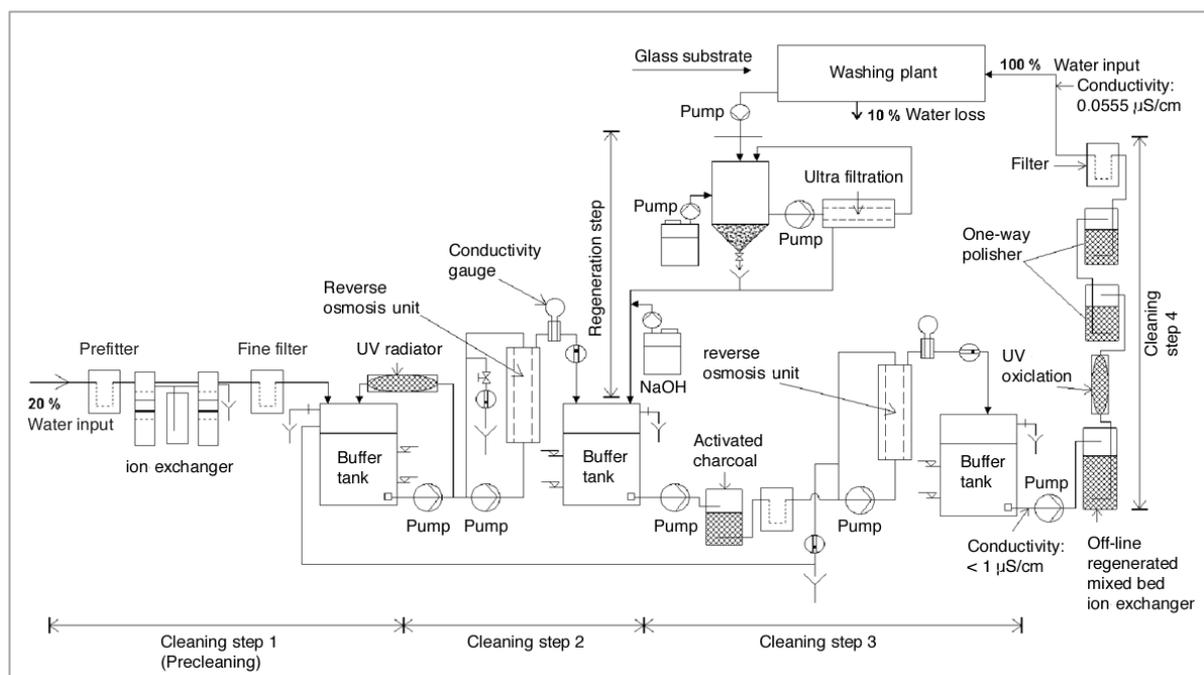


Figure 3.4.2.5 Water purification plant for the supply of highly-purified water for cleaning panes which are processed to flat displays

(source: FALK GMBH, Westerburg)

Figure 3.4.2.5 comprises four stages which are separated by three storage tanks. Because the impurities in the water are so manifold, several types of purification must be used. In a first stage, the water passes several filters and ion exchangers. Next, there are two stages which utilise the principle of reverse osmosis. Here the major inorganic substances, including silicic acid, and organic impurities, including germs, are removed. The exposure to UV rays aims to decompose organic substances of high molecular weight. To meet the strictest quality requirements, a fourth purification stage follows which consists of a cascade of

special ion exchangers combined with UV radiators. When purifying water for coating panes for construction and silver mirrors, this ion exchanger cascade is not necessary.

Drying methods for wet cleaning processes

All wet cleaning processes include a final cleaning zone where the panes are rinsed with highly-purified water, which means that their surfaces are wet. But all coating processes (except those which are based on the principle of chemical reduction and those which operate on-line with the flat glass production (see Chapter 4.3.1) require dry panes, so the flat glass panes must be dried before they enter the coating plant. To do so, the following methods can be used:

- Drying by displacing the water film with organic liquids
- Drying by dissolving the water film in organic liquids
- Drying with hot air
- Radiation heater drying
- Air blade drying

The selection of a suitable drying method depends on the cleaning process on the one hand and on the demands of the subsequent application on the other. Generally, it should be said that there are advantages and disadvantages to all the drying methods described here. Because of the low water-resistance of glass, drying the flat glass surface is also a critical process.

Drying by displacing the water film with organic liquids

This method uses organic fluids to seep under the water film of the wet pane and displace and finally separate it. The cleaned, wet panes are suspended from a holder and immersed into a bath filled with the drying fluid. Organic liquids with a relative density which is higher or lower than that of water are used as drying fluids. Once the panes are drawn out again, the organic fluid film vaporises and the panes are dry. Figure 3.4.2.6 shows a diagram of one of these drying plants.

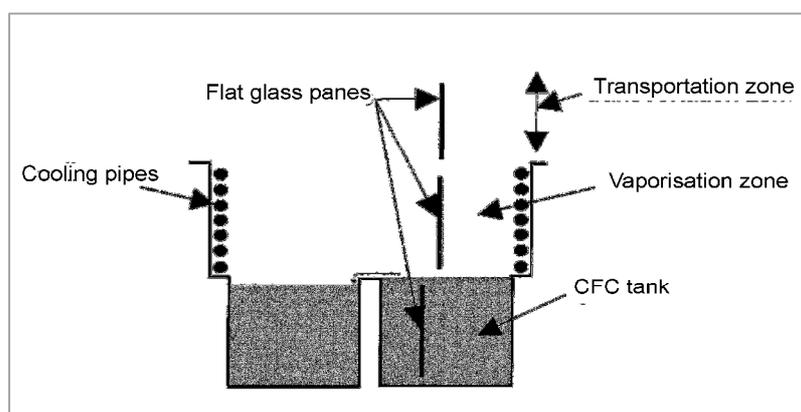


Figure 3.4.2.6 Diagram of a CFC drying plant

There are two drying possibilities which differ in the applied drying fluids. In the first case, using so-called dewatering fluids (DWF) with a higher density than water, the displaced water settles at the bottom of the bath and has to be removed from time to time. In the second case, using chlorofluorocarbons (CFCs, e.g. R 113) which are less dense than water, the displaced water floats on the surface of the bath and is transferred into a second bath, from which it is disposed of.

One disadvantage of DWFs is that they possess a relatively low vapour pressure, which means vaporisation takes a long time during which new contamination may occur. CFCs, on the contrary, vaporise from the pane surface within seconds, which is the great advantage of these drying agents. All CFCs, however, are hazardous to the environment so that they can only be used in closed-circuit plants, if their use is permitted at all.

Drying by dissolving the water film in organic liquids

With this drying method, the panes are also immersed in a bath of organic liquid. However, unlike the two cases discussed above, where the water film is separated from the pane, here it is molecularly dissolved. Once the pane is removed from the bath, the organic liquid together with the molecularly dissolved water vaporises off the pane surface and the pane is dry. Alcohols, especially isopropanol, are frequently used as drying agents for this process. Appropriate drying plants are usually similar to the one shown in Figure 3.4.2.6. The disadvantage here is the high flammability of the alcohols and hence the danger of explosion in such plants.

All drying plants which use organic liquids consist of three vertically arranged zones, as can be seen in Figure 3.4.2.6. There is an immersion zone, a vaporisation zone and a transportation zone for the transportation of the panes. Therefore, such plants are only economical to run for limited pane sizes. Drying plants operating on the basis of organic liquids are nowadays almost exclusively employed in combination with ultrasonic cleaning plants.

Hot air drying

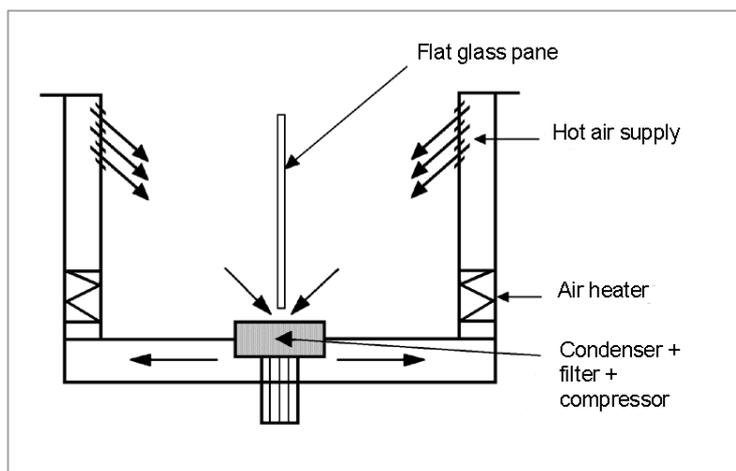


Figure 3.4.2.7

Diagram of a hot air drying

The principle of this drying method is based on the high capacity of hot air to absorb water. Figure 3.4.2.7 shows a diagram of a hot air drying plant. Hot filtered air sweeps over the cleaned, wet panes. The water film vaporises and the steam is removed by the air. If the air used is dehydrated by means of a condenser, it can be circulated. Hot air drying plants are environmentally friendly and are therefore often used instead of the above-mentioned types of drying plants which are environmentally harmful or combustible because they operate with organic liquids. But there is also a disadvantage to hot air drying plants. Because the panes have to be subjected to the hot air for a certain time, the glass surface may leach and panes may be marked by spots or strips of residues after drying.

Radiation heater drying

A special hot air drying method consists of drying the panes with a radiation heater. As shown in Figure 3.4.2.8, the wet pane is warmed with heating devices, e.g. infrared radiation, so that the water film vaporises. The steam is removed by a flow of air.

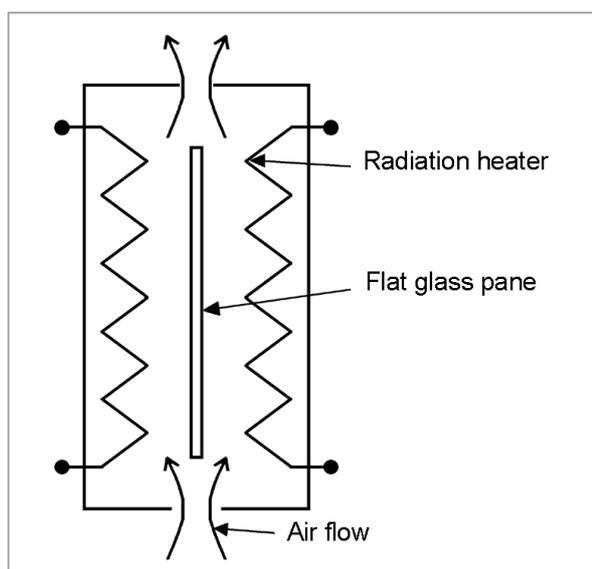


Figure 3.4.2.8:
Diagram of a radiation
heater drying plant

This drying method is rarely used to dry large flat glass panes. It possesses the same disadvantages as the hot air drying method described above.

Air blade drying

The air blade drying method is the most frequently used drying technique, especially for large panes. Figure 3.4.2.9 shows a diagram of this method. Compressed air reaches the wet pane surface through slit nozzles. These nozzles create an air flow like a knife blade so that the water film is separated from the pane immediately, then atomised and eventually removed together with the outgoing air. The compressed air must be very clean, i.e. it must be passed through special filters. The air blade drying method has a number of advantages. It ensures the quick removal of the water film and the panes remain cold. This, in turn, reduces the leaching effect and so the deposition of spots or stripes of leached-off materials on cleaned surfaces is kept to a minimum. Modern air blade drying plants are capable of

handling up to several million square metres of flat glass a year. They can be used to dry panes of any size up to 3.21 m x 6.00 m.

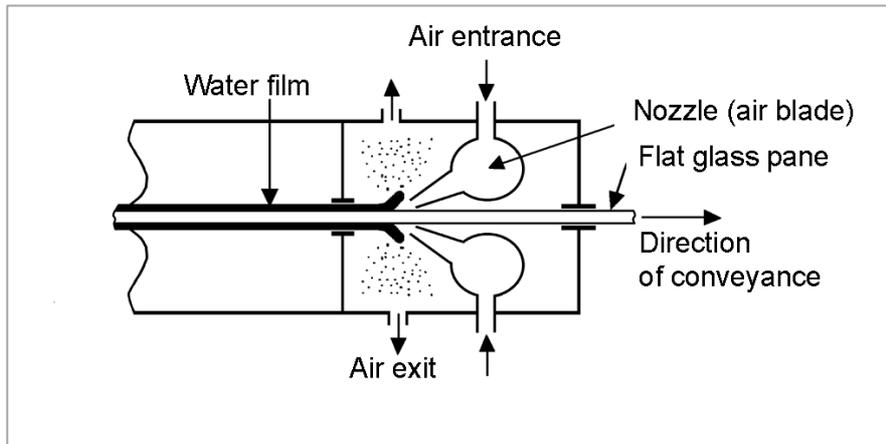


Figure 3.4.2.9 Diagram of an air blade drying plant

As mentioned above, the applied air must be very cleaned. The degree of cleanness, particularly the size and number of remaining particles per cubic metre, depends on the actual application. As regards the number of particles and germs, the purity degree of the drying air should be comparable to the quality requirements specified in Table 3.4.2.1 for the previously used cleaning water.

Thus it can be seen that there are both advantages and disadvantages with all drying techniques. Which is the best process for each coating depends mainly on the actual application, so that no general recommendations can be made here. However, brush cleaning combined with air blade drying has become the most common way of cleaning large area panes today.

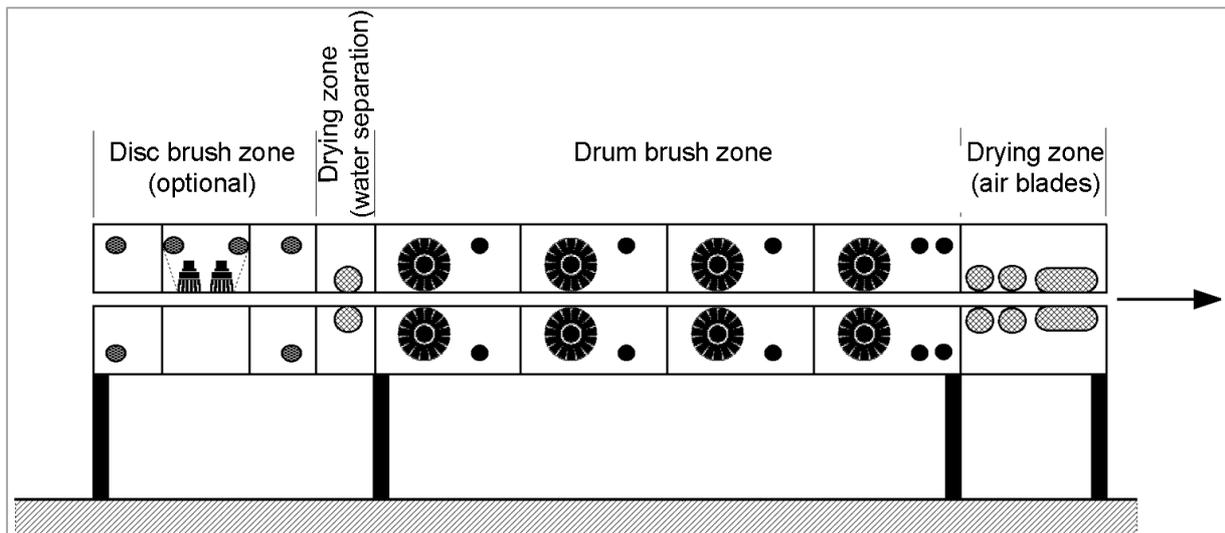


Figure 3.4.2.10 Diagram of a modern horizontal cleaning plant for large-area flat glass panes to be coated

(Source: Benteler AG, Bielefeld)

All types of drying installations in connection with wet cleaning processes are normally flanged directly to the exit of the cleaning plant. Figure 3.4.2.10 shows the diagram of a modern horizontal cleaning system and drying zone for large-area flat glass panes intended for subsequent coating.

3.4.3 Checking the pre-treated flat glass surfaces for coating

It is rather difficult to check the surface quality and cleanness of large-area glass panes on the production line after they have been washed and dried. The following means have been attempted to date:

- Wetting the surface with a thin dew water film and checking the condensation pattern
- Irradiation of the pane surface with focused light and checking the scattered light according to the 'dark field' principle

The first method has often been experimented with, but it has not yet been put into practical use. It is based on the fact that dirt particles, adherent in the corrosion layer affect the flat glass surface energy to which the steam condensation reacts very sensitively. In fact, this method is so sensitive that one can read the entire history of a pane, engraved, as it were in its corrosion layer. This can be done even with a very thin water film, by breathing onto the surface, for example. The difficulty with this testing method is, however, in distinguishing whether or not the surface impurities might have a negative effect on the subsequent coating process. Moreover, an automated evaluation of the condensed steam is not yet possible, so the water film has to be examined visually, which is a laborious task for large-area panes (e.g. 3.21 m x 6.00 m). This may be the main reason why this method has still not been adopted to check cleaned large-area panes.

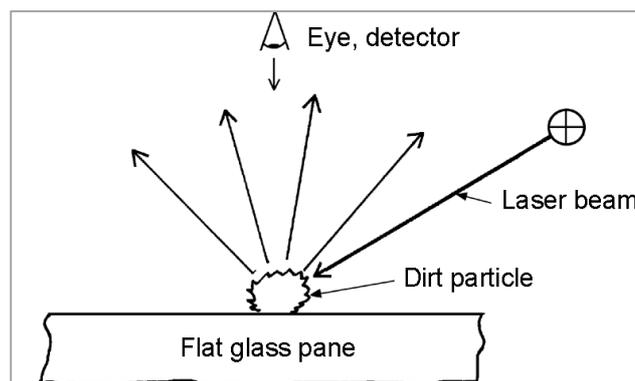


Figure 3.4.3.1 Operating principle of checking the surface cleanness by means of scattered light according to the 'dark field' principle

The principle of checking the pane surface cleanness by the second method is shown in Figure 3.4.3.1. Impurities on the pane surface generate diffuse light by scattering, which is detected.

Figure 3.4.3.2 shows a device which uses the principle of diffuse light detection. It has been developed for small panes, e.g. used as carrier plates for magnetic hard disks. This testing device, which is based on the dark field principle, scans the pane surface with a laser beam. When the beam strikes a clean area, the reflected beam disappears in a light trap. If the laser beam strikes an impurity, the light is reflected diffusely and can be determined with a detector. This device can be used to detect particles of less than 1 μm in size on the glass surface. However, it can only be used to check the surface contamination of flat glass samples with relatively small dimensions.

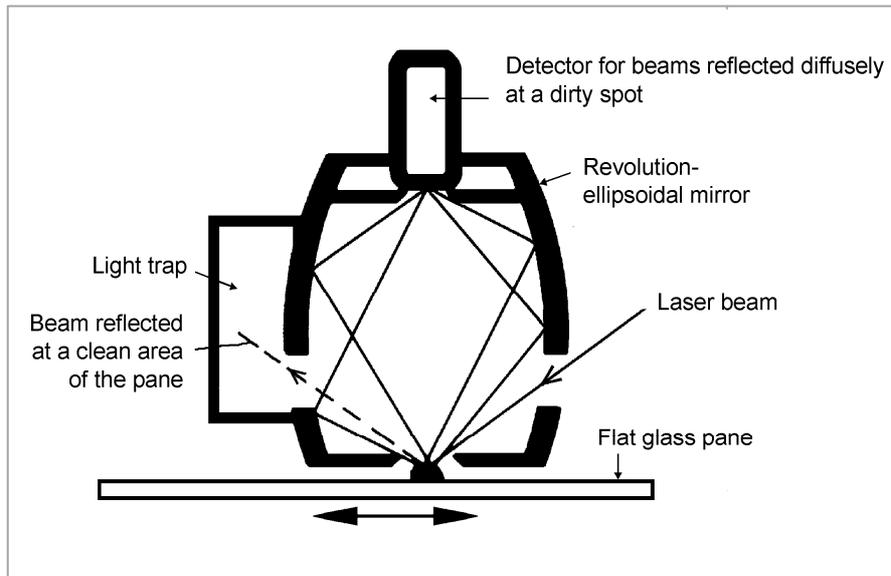


Figure 3.4.3.2 Diagram of an equipment to detect surface contamination of small flat glass samples by light scattering
(Source: LENHART and HÜLSING)

During the early years of coating large-area glass panes, when the effectiveness of cleaning prior to coating was very uncertain, a modified form of equipment based on the dark field principle was used in the production line for large flat glass panes up to an area of 3.21 m x 6.00 m. Figure 3.4.3.3 shows a schematic diagram of the inspection device that was used then.

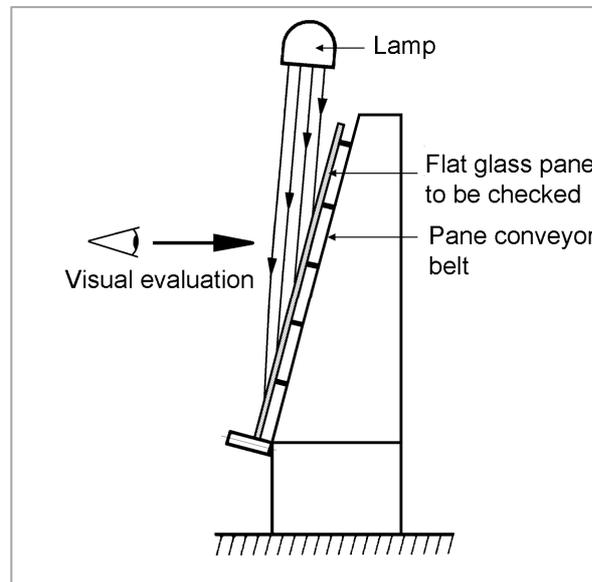


Figure 3.4.3.3:
Diagram of a cleanliness checking device for large panes

Of course, cleanliness can also be evaluated using surface analysis methods as described in Chapter 3.2.3. However, these techniques are only suitable for laboratory analysis of small glass samples and cannot be used in a production line.

Thus, it must be stated that it is not yet possible to reliably inspect the surface of large-area panes in a production line prior to coating. This is astonishing, considering that several hundred million m² of flat glass panes are coated annually around the world, quite often with very sensitive coatings.

Today, the most common means of supplying large-area flat glass panes for off-line coating purposes, i.e. independently of the flat glass manufacturing process, is to

- Use ‘virgin’ flat glass, i.e. glass which is either newly produced or properly preserved
- Clean the panes with an appropriate process and handle them carefully afterwards
- Ensure regular maintenance of the cleaning plant including the water purifying device
- Coat the glass panes immediately after cleaning and drying, and ensure clean pane conveyance within the plant
- Deposit a suitable blocking and adhesive layer onto the glass surface before applying the functional layer, thereby creating a ‘virgin’ surface artificially

It can be said that this deductive process for the preparation of large area flat glass surfaces intended for coating purposes has proved its reliability in practice regarding both quality and costs; for this reason it is practised around the world today.

4.0 Thin-film coating technologies for flat glass

4.1 Classification and requirements of thin-film coating technologies for flat glass

If thin film coating technologies are to be applied to flat glass on a commercial scale, they must be able to guarantee the following:

- Compatibility with the properties of flat glass
- Availability and usability of the coating material and the possibility for it to be processed as required by industrial-scale coating plants
- Feasibility to form sufficiently uniform layers on large surface areas
- Possibility of controlling the layer thickness
- Ability to achieve an adequate coating speed, or deposition rate, as it is termed by coating specialists
- Economic viability
- Environmental compatibility

This list of requirements considerably restricts the number of coating technologies which can be used on a laboratory scale.

Today, the thin film coating technologies used industrially for flat glass can be nearly exclusively classified as

- Vacuum processes also known as ‘physical vapour deposition’ (PVD)
- Chemical processes also known as ‘chemical deposition’ (CD)

In vacuum processes the coating material is evaporated under vacuum conditions and then condensed on a substrate surface. In chemical processes the coating material reacts chemically on the flat glass surface, usually at atmospheric pressure called atmospheric-pressure (AP) processes. In contrast, vacuum-based processes are also applied called low-pressure (LP) processes.

The technologies employed in vacuum flat glass coating processes basically comprise

- Sputter deposition, also called ‘sputtering’ applied normally
- Thermal vapour deposition applied only to a limited extent today.

Chemical coating technologies can be grouped into

- Coating by chemical reduction, by means of which the coating material, such as dissolved salt, is reduced on the flat glass surface to form a layer
- Coating by means of a chemical reaction on the hot surfaces, where the coating material reacts with certain reagents (e.g. air, oxygen, water vapour) under atmospheric pressure to form a layer. This type of coating is often known as pyrolytic coating, although this is not always an accurate description of the process. The common characteristic here is rather the chemical reaction on the hot glass surface. The coating material, which can be in vapour, liquid or solid (e.g. powder) form, comes

into contact with the hot glass surface. The three alternatives are known as chemical vapour deposition (CVD), liquid spray deposition and powder spray deposition. For some years now the latter method has no longer been employed for flat glass coating applications.

- Sol-gel deposition, by means of which the layers are also formed by the effect of heat. The coating process, however, is a three-step process. In the first step, the coating material, the as-called sol, is deposited as a liquid film onto the flat glass surface at room temperature. In the second step, this liquid film is transformed into a gel film by hydrolysis also at room temperature. In the third step, the gel film is densified to become a solid layer by application of heat with a firing process. Nowadays dipping techniques are almost exclusively used in order to apply the liquid film onto the flat glass surface.

In addition to the above-mentioned processes, another process which has become increasingly important in recent years is 'plasma-assisted CVD' (PACVD), also known as 'plasma-enhanced CVD' (PECVD). This CVD process is carried out at low pressure, combined with a gas discharge process. Therefore, PACVD (PECVD) has to be categorised as a separate group, fitting in between vacuum processes and chemical deposition.

In some cases, float glass panes are coated immediately after production by a chemical reaction process on the hot glass surface. This combination of production and refinement is called 'on-line coating', whereas coatings applied independently of the flat glass production process are called 'off-line coating'.

Commercial-scale flat glass coating with thin films began in the late 1950s and early 1960s. It is based principally on scientific discoveries of the inter-war period. H. MAYER, L. HOLLAND and W. GEFFKEN were among the pioneers in this field.

4.2 Vacuum processes employed for flat glass coating

4.2.1 Sputter deposition

4.2.1.1 Applications of the sputtering process for flat glass coating

Sputtering has gained greater importance economically than any other flat glass coating technique in use today. World-wide, several 100 million m² of flat glass are coated each year by sputtering and this amount is increasing steadily. Sputtering is mainly used in the manufacturing of

- Low emissivity layers, e.g. for heat-insulating glass
- Layers which provide protection from solar radiation, i.e. for solar-control glass
- Anti-reflection layers for various applications
- Transparent electrodes for electrically conductive glass, e.g. for heatable glass, shielding glass for electromagnetic radiation or electrical devices made from or using flat glass

In addition, sputtering is also used for mirror layers and electrochromic layers, although less extensively. Today, sputtered layers are used mainly for optical and electrical functions.

Typically, materials which are applied commercially using sputtering processes include

- Metals, such as silver, gold, nickel chromium, stainless steel and aluminium
- Semiconductors, such as indium oxide doped with tin and, more recently, zinc oxide doped with aluminium or boron
- Low-absorption dielectric layers: bismuth oxide, tin oxide, zinc oxide, zinc stannate and, more recently, titanium oxide, silicon oxide and silicon nitride
- Electrochromic materials, such as tungsten bronze

By combining coatings of these materials, i.e. through the use of so-called layer systems, the above-mentioned functions of flat glass can be achieved.

Because the coating materials can only be sputtered in vacuum conditions, sputtering processes for flat glass are necessarily performed off-line, i.e. independently of the glass production. However, being an off-line process, sputtering allows for a high level of flexibility, as regards the layer system (and thereby the functionality of the coatings applied) and, therefore, the scale of products. Another great advantage of sputtering is that it is generally regarded to be environmentally compatible, since no waste products are created which are difficult to dispose of.

The above list of the application of sputtering is not exhaustive. It is expected that this technique will be used in different applications and for new functions in the future.

4.2.1.2 The principles of sputter deposition

The deposition of layers by means of sputtering was discovered in 1852 by W. R. GROVE in Britain and in 1858 by J. PLÜCKER in Germany, while they were experimenting with glow discharge processes. Sputtering is based on a gas discharge, known as the 'plasma', which is ignited at low pressure and then interacts with the coating material, known as the target. In this process the coating material is eroded from the target surface and condensed as a layer on a substrate, in this case the flat glass pane, which is positioned near the target. This is what is meant by sputtering.

The deposition of a material by means of a gas discharge is well-illustrated with the example of a fluorescent lamp. A fluorescent lamp consists of a tube which is filled with gas at a low pressure. Each end of the tube is fitted with an electrode, to which an alternating current is passed. The gas discharge is ignited and light is emitted. In front of the electrodes a dark space is visible, approximately 1 cm in length. Here, after many operating hours, a dark metallic layer is deposited onto the inner tube wall. This metal layer consists of material, which is eroded from the electrode surface during the gas discharge process. A similar process takes place during sputter coating.

A gas discharge takes place with an ionised gas consisting of free charge carriers, i.e. ions and electrons, as well as electrically neutral gas atoms. Figure 4.2.1.2.1 shows a diagram of the current/ voltage curve of a gas discharge in argon at a pressure p of approximately $5 \cdot 10^{-2}$ mbar, i.e. under vacuum conditions. This characteristic curve can be measured with

the help of the circuit shown next to the diagram which consists of a power supply U_B , a variable load resistor R_L and the gas discharge arrangement. The sputtering process is run in the current range of anomalous glow discharge. Only under this condition sputtering does run stably. At higher currents an arc discharge takes place, which is not desired for sputtering. However, both current ranges permit the gas discharge to run as a self-sustaining process, i.e. without ionising effects from outside the system. The working point U_A/I_A of sputtering is adjusted with the variable load resistor R_L which also aims to avoid the discharge becoming an arc discharge. It is of vital importance to avoid arc discharges when sputtering because there is a risk of damage to the target and also the deposited layer. It should be noted that the current/ voltage characteristic of the gas discharge is a non-linear curve. This has consequences for designing medium frequency AC sputtering arrangements (see also Chapter 4.2.1.5.2).

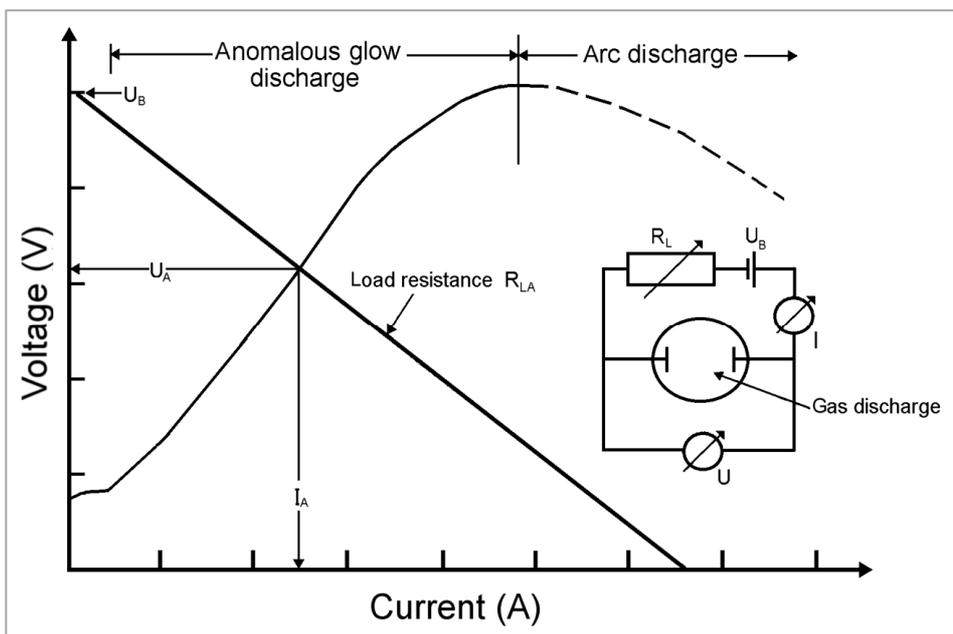


Figure 4.2.1.2.1 : Diagram of the current/ voltage curve of an argon gas discharge at a pressure of p approximately $5 \cdot 10^{-2}$ mbar

Figure 4.2.1.2.2a shows the structure of a gas discharge for argon taking into account the conditions explained above. In front of the negative electrode, the cathode, there is a brightly glowing space, the cathode glow area, followed by the dark space mentioned above. Beyond this, towards the positive electrode, the so-called anode, there is a brightly glowing zone, which would be the luminous zone in a fluorescent lamp. Just in front of the anode another bright rim of light can be seen, the anode glow area.

Measuring the electric potential of the gas discharge between cathode and anode gives the voltage curve shown in Figure 4.2.1.2.2b from which it is evident that the voltage drops entirely across the dark space. This voltage drop occurs because positive argon ions are drawn from the edge of the brightly glowing zone towards the cathode. As the argon ions collide with the cathode, material is eroded from the cathode surface, i.e. sputtered, and electrons are released at the same time.

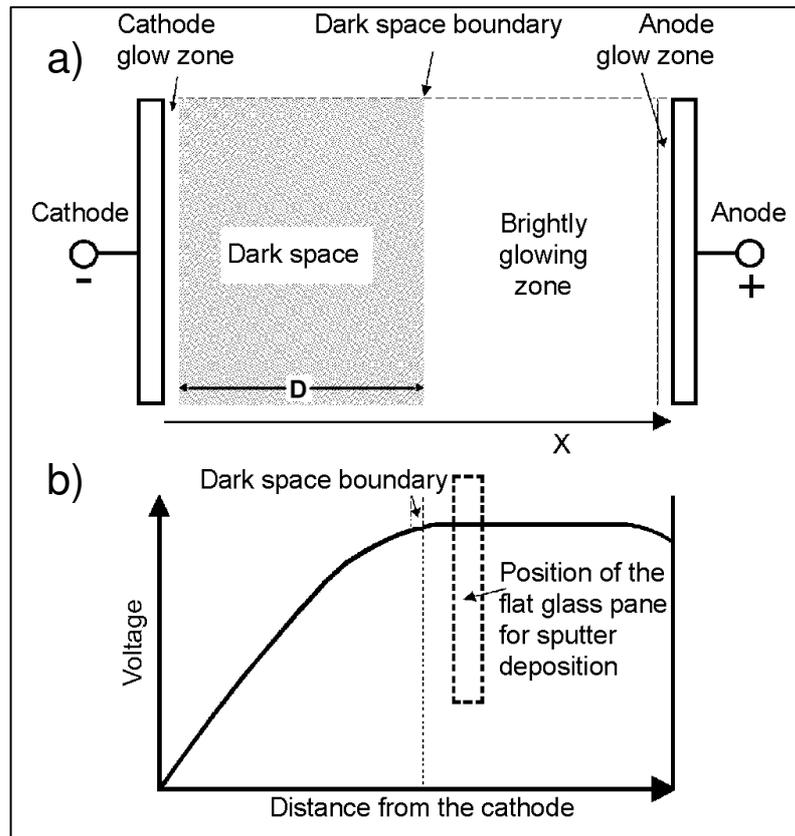


Figure 4.2.1.2.2: Schematic design of
 a) the structure
 b) the voltage curve of a DC argon gas discharge at $p = 5 \cdot 10^{-2}$ mbar

These electrons are accelerated by the voltage drop across the dark space and move into the brightly glowing zone where they collide with argon atoms generating argon ions. In the brightly glowing zone, the number of positive and negative charge carriers (argon ions and electrons), is equal and almost constant. The degree of ionisation of the gas atoms is not very high (about 1 %). The luminous effect in this zone is caused by a release of energy as excited argon atoms are transferred into a state of lower energy, a process which is referred to as 'relaxation luminescence'.

The very bright light at both electrodes results from positive argon ions and negative electrons colliding on the electrode surface, whereby neutral argon atoms are generated and light is emitted. This type of light generation is called 'recombination luminescence'. Charge carriers which drift away from the discharge or are eliminated by recombination are replaced by the ionisation of argon atoms through collision with released electrons (see above). This ionisation works at the same pace as the recombination so that the gas discharge is self-sustaining once ignited.

Enlarging the distance X between anode and cathode at constant low pressure and constant voltage results in the expansion of the brightly glowing zone, whereas the dark space width D remains unchanged. For sputter deposition, the substrate, in our case the flat glass pane, is positioned in the brightly glowing zone, about 5 mm away from the boundary of the dark space, as can be seen in Figure 4.2.1.2.2b. Then, a bright rim of light becomes visible right in front of the pane, which is also caused by recombination

luminescence. If the substrate is positioned in the dark space, the impulse of the electrons released at the cathode is too weak to ionise argon atoms in the brightly glowing zone and the discharge process cannot take place. However, this effect is employed to suppress the discharge in regions where it is not desired, e.g. to shield the cathode (see Figure 4.2.1.3.1).

The width of the dark space depends on the pressure at which the gas discharge glows, the voltage, the density of gas ions and the number of electrons released from the cathode. The higher the pressure, the voltage, the density of gas ions and the number of electrons, the narrower the dark space and vice versa.

The light of the discharge can be used to diagnose the sputtering process with the help of plasma emission monitoring (PEM) (see also Figure 4.2.1.5.2.13).

4.2.1.3 Sputter deposition in a non-reactive atmosphere

Non-reactive sputtering means that the sputtering gas does not react chemically with the coating material during sputtering. Therefore inert gases, preferably argon, are used for non-reactive sputtering. In contrast to non-reactive sputtering, chemical reactions involving the sputtering gas play an important role in reactive sputtering; this process is explained in the following Chapter.

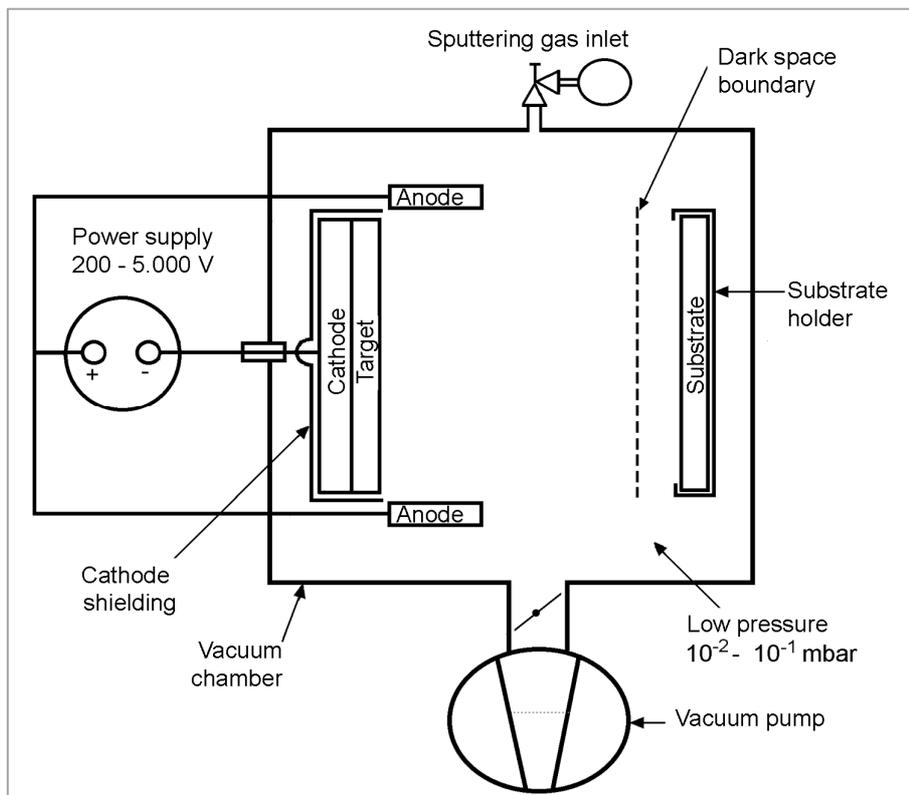


Figure 4.2.1.3.1: Diagram of a sputtering chamber

Figure 4.2.1.3.1 shows a diagram of a sputtering plant. A sputtering plant consists of a vacuum chamber, a sputtering gas inlet valve, a set of vacuum pumps which maintain a working pressure of 10^{-3} to 10^{-1} mbar, and the sputtering equipment which comprises a cathode with the coating material, the so-called 'target', and an anode. The gas discharge is ignited with a direct current at a voltage of 200 to 5,000 V, generated by a power supply

unit. The substrate to be coated is positioned in front of the target, beyond the boundary of the dark space, on a substrate holder. The sides of the cathode not facing the substrate are shielded by earthed metal sheets which are positioned in the dark space.

Non-reactive sputtering with DC voltage or low-frequency AC voltage at frequencies between 50 and 100,000 Hz, as used for flat glass coating, requires targets with sufficient electrical conductivity, e.g. metals, since the electric circuit, which passes from the cathode through the target and the gas discharge to the anode is otherwise interrupted and the discharge does not take place.

The gas discharge fulfils two functions in the sputtering process. First, ions are generated which, secondly, erode the coating material from the target surface. The individual processes which take place during sputtering on the target surface, in the gas discharge and on the substrate are manifold, and they are described here only insofar as it is deemed necessary in order to understand the sputter deposition process. For in-depth studies of the physical principles, readers are referred to literature detailed in the References (FREY/KIENEL, HAEFER, STOLLENWERK).

Figure 4.2.1.3.2 shows the basic individual processes of sputtering with a metallic target in an argon atmosphere.

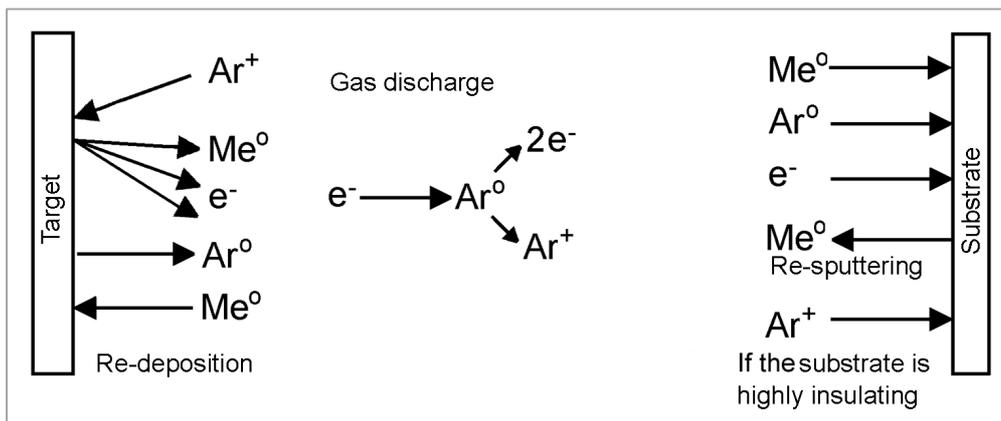
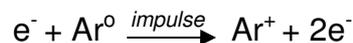


Figure 4.2.1.3.2: Sputtering processes with a metallic target in an argon atmosphere

The collision ionisation, i.e. the ionisation by impulse transfer from the electrons (e^-) to the neutral argon atoms (Ar^0), is the most important process of the gas discharge. This collision ionisation is described by the reaction equation:



The argon ions (Ar^+) produced in this process cause the sputtering process on the target surface. The electrons (e^-) produced at the target and in the gas discharge impinge on all surfaces around the cathode and so also on the substrate.

On the target surface, the following processes can be observed. The positive argon ions (Ar^+) are accelerated by the voltage drop in the dark space, bombard the target and erode metal particles from its surface through a mechanical collision, i.e. by an impulse transfer. The metal particles consist of either one (Me , 80 %) or two atoms (Me_2 , 20 %). This process can roughly be compared to sand-blasting a surface. About 99 % of the metal particles are electrically neutral (Me^0), only a very small portion ($\leq 1\%$) are charged positively or negatively. At the same time, the target surface reflects neutral argon atoms (Ar^0), which

are generated by neutralisation of incident Ar^+ ions during the collision, and which still possess 20 % to 30 % of their previous energy. Furthermore, electrons (e^-) are released, which are necessary to sustain the gas discharge. When metallic targets are used, on average one electron is released per ten incident argon ions. Some of the sputtered metal particles decelerate because of collisions with particles of the gas discharge in front of the cathode. The decelerated particles diffuse back to the target surface and condense there. This effect is referred to as re-deposition (RD). It influences the temporal behaviour of the target.

The most important processes on the substrate surface are the condensing of the sputtered particles (Me^0) to form a layer, the collision of argon atoms (Ar^0) and electrons (e^-) with the surface or coating and the eroding of particles from the substrate surface and the coating. This last process is called re-sputtering (RS). It occurs due to the fact that the sputtered particles (Me^0) have an average energy of 4 eV with peak values of up to more than 50 eV and that they are therefore subject to material erosion by impulse transfer, as is the case on the target. Neutral argon atoms (Ar^0) which are reflected at the target also contribute to the re-sputtering process. The released particles decelerate when they collide with particles in the gas discharge zone and in part condense on the substrate. If they are not deflected (see Chapter 4.2.1.5.2), the incident electrons heat up the substrate, which is a negative side effect, especially for heat-sensitive substrates.

The way the condensed layers grow is influenced by the substrate surface being bombarded with highly energetic particles and possibly also electrons. This bombardment can have both negative and positive consequences for the growth of the layers. Among the positive effects are that the adhesion of the sputtered layers to the substrate improves, and that gases desorb from the substrate surface and the layer, resulting in layers which are 'pure' as well as compact and, some times, highly crystalline. However, there are also negative effects, e.g. the interfaces between the individual layers within a layer system become blurred and indistinct. This is caused by so-called 'ion milling', i.e. when adjoining layers are mixed by incident, highly energetic ions. Ion milling can have a negative effect on various properties of layer systems.

If the substrate is a flat glass pane, another important effect should be mentioned. Since flat glass is a good insulator of electricity, its surface becomes charged as a result of electron and/ or ion bombardment, leading to a difference in potential between the pane and the gas discharge; specialists speak of a 'floating' potential of the substrate. The potential difference can amount to some 10 V so that argon ions (Ar^+) are accelerated towards the flat glass surface. This also results in an intensification of positive and negative effects which occur when highly energetic particles collide with the pane surface, as explained above.

The sputtered particles condense not only onto the substrate but also onto surfaces around the cathode, e.g. onto the anode or the vacuum chamber walls. Figure 4.2.1.3.3 shows the distribution of the particle current density F of the sputtered particles and its portions. The particle current density can be calculated according to the equation

$$F = F_S + F_A + F_W$$

with F_S being the portion towards the substrate, F_A that towards the anode and F_W that towards the walls of the vacuum chamber. The particle current portions F_A and F_W are lost for the coating process. Because they cause electrically conductive layers, they do not

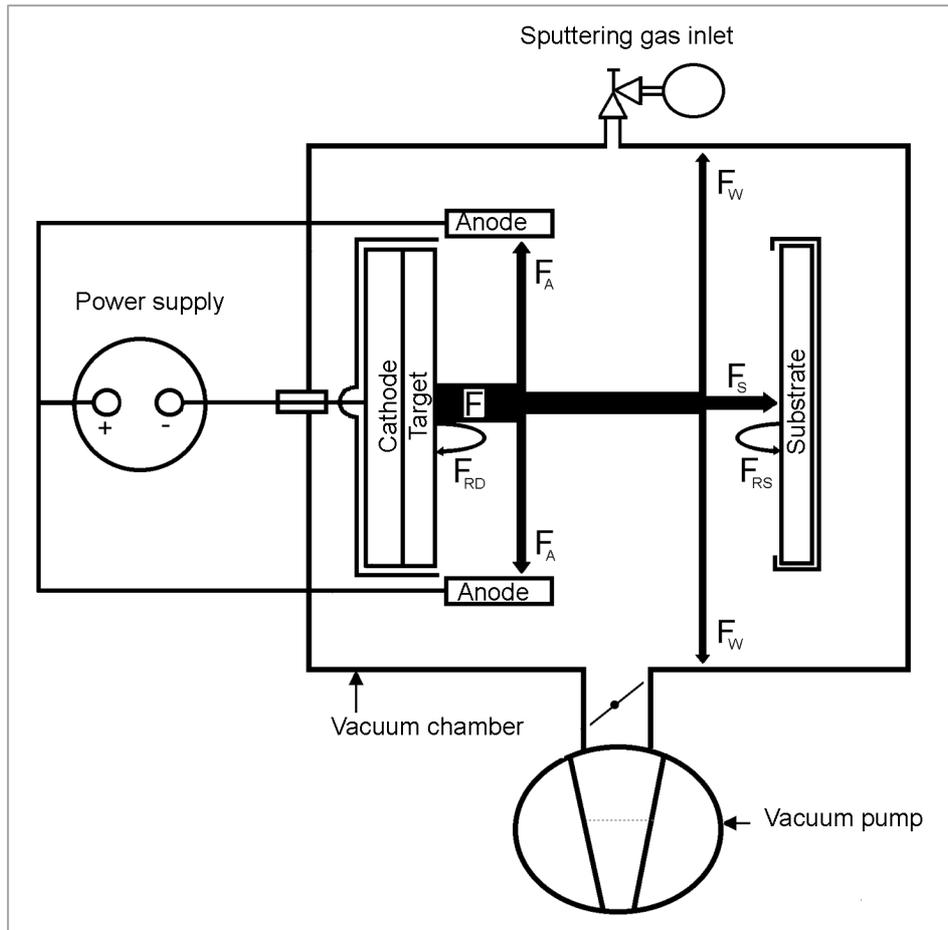


Figure 4.2.1.3.3: Distribution of the particle current density F sputtered from the target surface

disturb the sputtering process in contrast to reactive sputtering, as will be seen in Chapter 4.2.1.4). As has been seen above, the re-deposited particle current portions F_{RD} and F_{RS} have an effect on both the temporal behaviour of the target and the growth of the layer, but not on the balance of the particle current density.

When sputtering metal alloys, such as NiCr or stainless steel, the processes on the target surface are similar. The material released from the target is mainly in the form of single atoms and, to a lesser degree, diatomic molecules, consisting of either identical or non-identical atoms. The great advantage of the sputter deposition is that alloys can be deposited stoichiometrically. After a preliminary burn-in period for the conditioning of the target surface at the beginning of the sputtering process, the chemical composition of the layer is exactly the same as that of the target material. Normally, no separation of the material mixture is observed, as is known from thermal vapour deposition in particular.

Electrically conductive oxidic materials, such as tin-doped indium oxide (ITO) (see Chapter 5.1.2.1, Part II), can also be sputtered at DC voltage. As well as metal atoms (Me^0) and metal oxides (MeO^0) in neutral form, molecular oxygen (O_2) and negative oxygen ions (O^-) are also released. Because released oxygen is constantly being removed e.g. by pumping during the sputtering of oxides, a corresponding amount of fresh oxygen must be admitted to the sputtering gas argon so that the deposited layer grows stoichiometrically.

The number of sputtered particles per argon ion incident upon the target, the so-called sputtering yield S , is of interest economically, because it forms a measure for the maximum

possible coating rate. The sputtering yield depends on the energy of the argon ions colliding with the target but also on the surface bonding energy of the target material (the sublimation energy), its crystalline structure and other surface conditions, i.e. the sputtering yield depends mainly on the material.

The higher the atomic mass of the incident ions, the higher their energy, provided the sputtering voltage is constant. For non-reactive sputtering, it is predominantly inert gases which are used as sputtering gases, as has been mentioned above. Of the possible gases, xenon would be the most suitable, because of its high atomic mass of 131. However, for economic reasons, inexpensive argon, with an atomic mass of only 40, is used for commercial-scale sputtering processes.

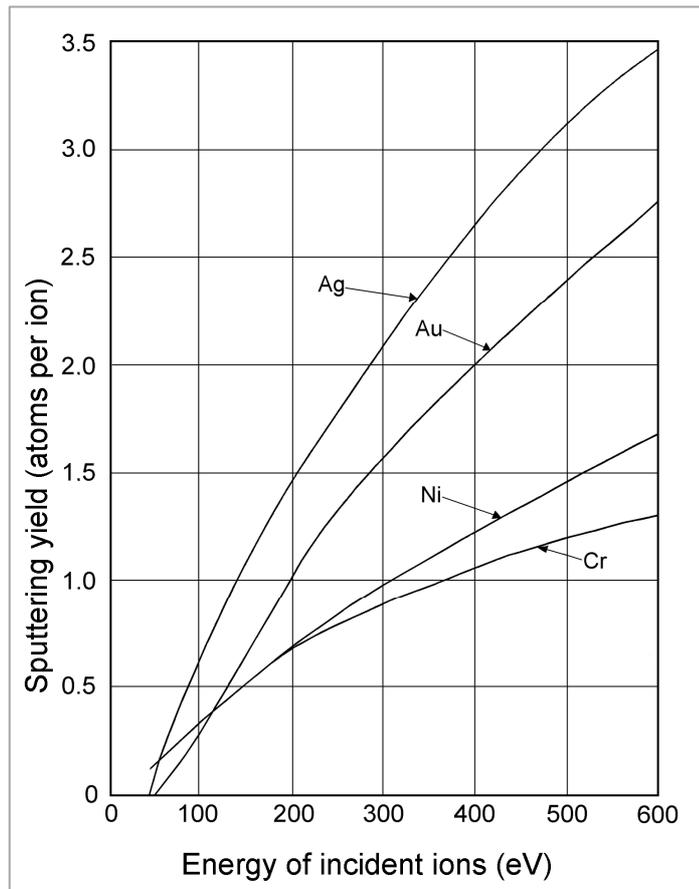


Figure 4.2.1.3.4:

Sputtering yield of several metals dependent on the energy of the incident argon ions

(source: GENERAL MILLS REPORT 2309, 1962)

As can be seen from Figure 4.2.1.3.4, the sputtering yield for a certain material, e.g. silver, increases with the energy of the incident ions, in this case argon ions, i.e. with an increasing cathode voltage. The energy of the incident ions must exceed a certain threshold value, in order for the sputtering process to start at all. This threshold value depends on the sublimation energy of the material to be sputtered, i.e. it is also dependent on the material. The starting value is typically between 5 and 30 eV. Figure 4.2.1.3.4 shows the sputtering yield depending on the energy of the argon ions for several metals which are used in flat glass coating technologies.

It can be seen that the sputtering yield varies considerably. Gold (Au), silver (Ag) and copper (Cu) have a high sputtering yield, whereas nickel (Ni), chrome (Cr) and iron (Fe) have a much lower one. It should be noted that the sputtering yield also depends on the angle of incidence of the argon ions and, to a lesser degree, on the target temperature.

The gravimetric deposition rate of the layer on the substrate, the so-called sputtering rate R_m , is linked to the sputtering yield. R_m is the product of the sputtering yield S , the ion current towards the cathode j , the mass of the sputtered particles m , the ratio of the substrate surface area A_S to that of the total surface A onto which the particles may be deposited (see Figure 4.2.1.3.3), and the sticking coefficient α_S of the particles on the substrate or layer. From this the following equation can be drawn:

$$R_m = \alpha_S \cdot j \cdot S \cdot m \cdot A_S / A \quad [\text{g}/\text{cm}^2 \cdot \text{s}].$$

If the gravimetric sputtering rate R_m of a homogenous layer is divided by the specific weight ρ of the deposited material, the resulting figure is the geometric sputtering rate R_d . It follows:

$$R_d = R_m / \rho \quad [\text{nm}/\text{s}].$$

In some textbooks, this is sometimes confusingly also referred to as the sputtering rate.

Both R_m and R_d depend on the material-specific parameters S and m , the process parameter j , the plant-specific parameters A_S and A , the substrate properties and the energy of the incident particles. The latter value also influences the sticking coefficient α_S . A comparison of the parameters R_m and R_d , measured in different processes and at different coating plants is therefore very difficult because A_S , A and α_S may differ as well. The only definite value is the sputtering yield S , depending on the energy of the incident ions. If the sputtering yields S for different materials are compared, e.g. as published in the General Mills Report 2309, the deposition rate can be estimated, and thus also the economic viability of an intended production with a given plant concept.

As has already been demonstrated above, the deposition rate and the structure of the layers are determined by the sputtering process. According to studies by MOVCHAN and DEMCHISHIN, three individual zones of different layer structure can be distinguished in case of the thermal vapour deposition process. The layer structure ranges from porous and acicular at low temperatures to coarse crystalline at high temperatures. The transition temperatures between the individual zones depend on the substrate roughness, the diffusion rate of the sputtered atoms onto the substrate surface and into the layer, as well as on the bonding energy between the sputtering material and the substrate. With sputtering, a downward shift in these transition temperatures of the individual zones is observed, as the energy of the incident particles increases. At the same time, as working pressure increases, there is an upward shift in the transition temperatures. This was discovered during studies carried out by THORNTON.

The adhesion energy (see also Chapter 5.5.1, Part II) of metals which are frequently used for flat glass coating (chrome, nickel chromium, stainless steel and aluminium) and the diffusion rate of the particles incident on the substrate with very high energy are so high that the result is a deposition of a uniform, homogenous, compact and quasi crystalline layer, after an oxidic transition layer which is formed due to the ion milling effect (see above). For gold and silver coatings on flat glass, it is a different story, as will be discussed in more detail in Chapter 5.1.2.2, Part II. In this case the adhesion energy, and hence the adherence to and wettability of the glass surface, are so low that the layers do not grow uniformly, but go through several discontinuous steps as the deposition advances. The use of appropriate adhesion layers between the glass surface and the gold or silver layers enhances the uniform growth of the latter (see Chapter 5.1.2.2, Part II).

4.2.1.4 Sputter deposition in a reactive atmosphere

Reactive sputtering means that the coating material is sputtered in an atmosphere of reactive gases. It differs from non-reactive sputtering in that the sputtering gas reacts chemically with the target material during the sputtering process. Reactive sputtering enables coating of electrically non-conductive, i.e. dielectric materials, to be deposited on the basis of oxides, nitrides and oxynitrides. The layers of these dielectric materials are used in flat glass coating processes as adherence-enhancing, protective, reflection and anti-reflection layers. Reactive sputtering is also applied to deposit electrically conductive oxide layers, so-called semiconductor layers, such as are required for the production of electrically conductive glass and glass panes with a low-emissive surface (see discussion in Chapter 5, Part II).

The design of sputtering plants for reactive sputtering is identical to that for non-reactive sputtering (see Figure 4.2.1.3.1). The target is again made from electrically conductive materials, such as bismuth, tin, zinc and titanium, or semiconductors, such as ITO (see Chapter 5.1.2.1, Part II) or conductive silicon. Reactive sputtering differs from non-reactive sputtering in that reactive gases are added to the sputtering gas argon. Oxygen is added to deposit oxide layers, nitrogen is added to deposit nitride layers, and a mixture of both gases is added to deposit oxynitride layers. Similarly, methane (CH_4) can be added for the formation of carbide layers and hydrosulphide (H_2S) for sulphide layers. However, these two types of layers are as yet not used commercially for flat glass coating. Due to the added reactive gases, the processes which take place on the target surface, in the gas discharge zone and on the substrate surface are more numerous than in the case of non-reactive sputtering. In addition, various processes which take place in the vicinity of the cathode also play an important role in the sputtering process.

The following example of oxidic sputtering should illustrate the phenomena of reactive sputtering, insofar as is necessary in order to comprehend this process. To gain a deeper insight into the subject, the work of STOLLENWERK (detailed in the References) is recommended for further reading. Excited by the gas discharge, the oxygen colliding with the target reacts with the target surface, as a result of which an oxide layer is generated on it. Due to a mechanical impulse of the ions accelerated in the dark space onto the target surface (in the case of reactive sputtering these are argon ions (Ar^+) and oxygen ions (O^{2+})), metals (Me), metal oxides (MeO), oxygen molecules (O_2) and negative oxygen ions (O^-) the target is eroded. All these particles have a very high energy, as was demonstrated in Chapter 4.2.1.3. As with non-reactive sputtering, the particle current F of the sputtered material condenses onto the substrate and onto all the other surfaces surrounding the cathode, i.e. the anode and chamber walls (see Figure 4.2.1.3.3). In addition, the collision of ions with the target surface causes electrons (e^-) to be released. However, in contrast to non-reactive sputtering, the number of released electrons is much higher: one incidental ion causes up to five electrons to be released, which has a major effect on the gas discharge. Compared to sputtering in a pure argon atmosphere, the dark space zone is narrowed, the cathode voltage decreases and the cathode current increases, provided the sputtering pressure p remains constant. From this, it follows that the density of the charge carriers in the gas discharge is much higher in the case of reactive sputtering than with non-reactive sputtering.

Because of the constant erosion and generation of the oxide layer on the target surface, the electric circuit of the discharge is not interrupted. However, the material condensing onto the anodes is, in contrast to the non-reactive process, electrically insulating and can accumulate to such an extent that it eventually interrupts the electric circuit of the gas discharge. This affects the electric potentials in the gas discharge and hence the sputtering process itself, as well as the properties of the deposited layer, e.g. the optically effective refractive index. The anode appears gradually to fade more and more, which is also described as the 'disappearing anode effect'. Because in the case of non-reactive sputtering the material condensing onto the anode is electrically conductive, this effect is not observed.

There is another phenomenon which has a considerably greater influence on the reactive sputtering process than it does on the non-reactive process. This is the re-deposition of the sputtered material on the target surface. The re-deposited oxidic material builds up electrically insulating layers on the target beside the erosion zones. During the sputtering process, electrical charges accumulate on these re-deposited layers through incident positive ions, which changes the electrical potential on the target surface, resulting in an arc discharge, known as 'arcing' (see Chapter 4.2.1.5.2), whereby the target and possibly also the coating can be damaged or even destroyed. This is one cause of arcing during reactive sputtering. Special electronic circuits, fitted in the power supply units for the plasma generation, have been developed to weaken the effects of an arc discharge by blanking out the power supply for a very short period.

Reactive sputtering is characterised by one further phenomenon, which is demonstrated by the diagram in Figure 4.2.1.4.1. The sputtering rate curves show a mismatch according to whether the amount of the reactive gas admitted during the process is increased or decreased. This effect is called the 'hysteresis' effect.

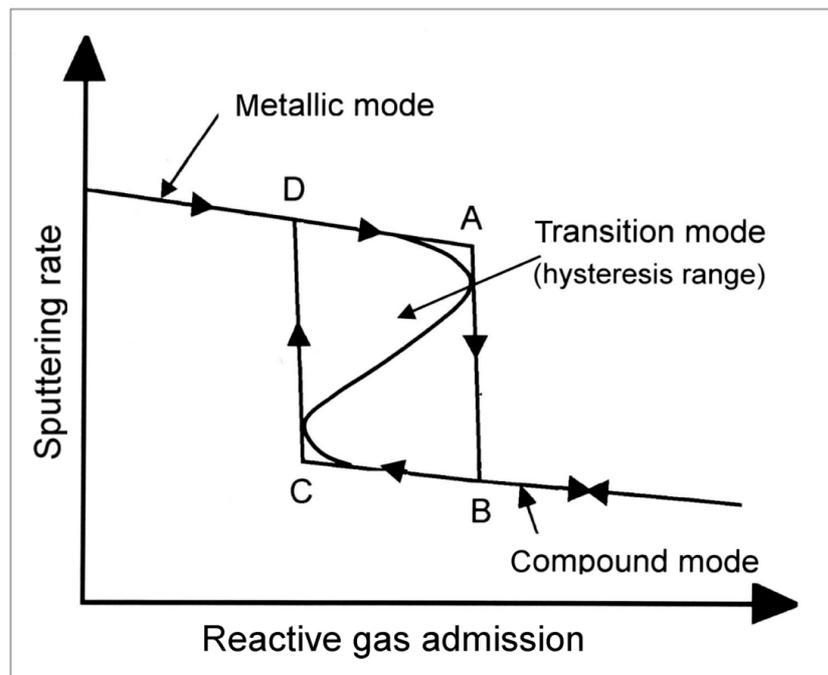


Figure 4.2.1.4.1:
The hysteresis effect
during reactive sputtering

From Figure 4.2.1.4.1 it can be seen that, when a small amount of the reactive gas is admitted, the sputtering rate R_m is nearly identical to that of the metal. This is called the

'metallic mode'. If the amount of reactive gas admitted is further increased, the sputtering rate curve drops steeply at point A and reaches the level of oxidic sputtering, the so-called 'compound mode', at point B. If the amount of reactive gas admitted is reduced again, the sputtering rate does not rise at point B, but only later at point C, in order to reach point D (the metallic mode), before point A. In the past, it was not possible to control the gas discharge precisely enough to sputter in the hysteresis range, also called the 'transition mode'. However, because of very efficient gas discharge control devices available today for power supplies and admission of the reactive gas, working points on the S-shaped section of the curve in the transition mode shown in Figure 4.2.1.4.1 have become feasible. By taking advantage of the improved gas control equipment, the sputtering rate of materials which can only be sputtered with difficulty in the compound mode can be increased.

For a deeper insight into the hysteresis effect, it is necessary to look at the distribution of the reactive gas q which has been admitted, as shown in Figure 4.2.1.4.2.

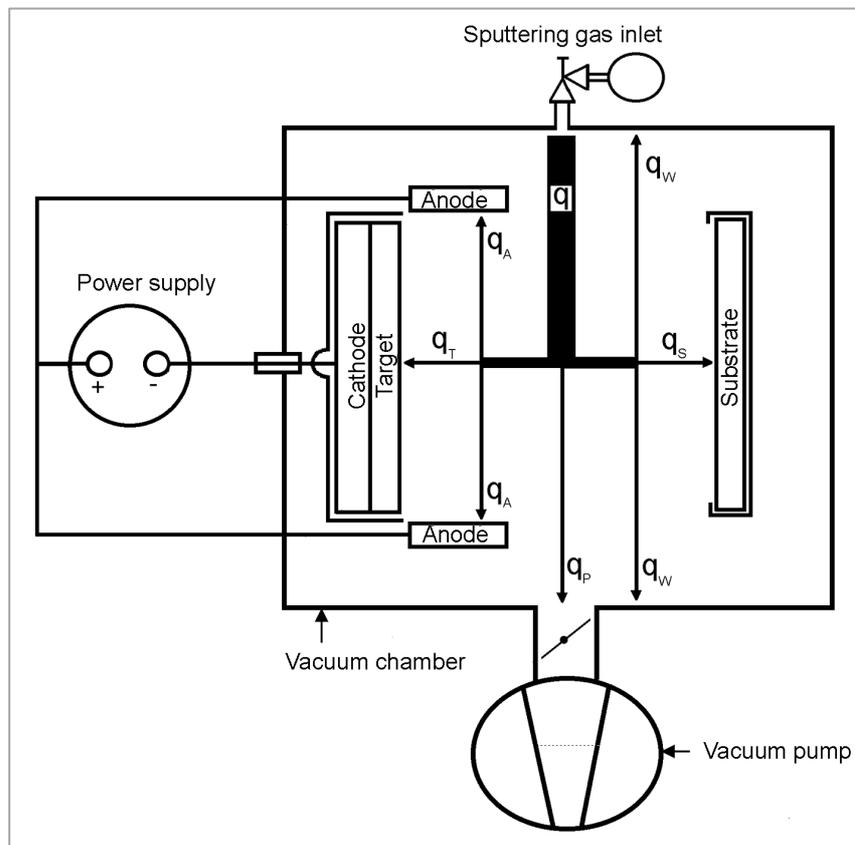


Figure 4.2.1.4.2: Distribution of oxygen admitted into the vacuum chamber

In this example oxygen is used. A portion of the oxygen admitted reaches the target (q_T) and causes the reactive sputtering process. Another portion reacts with the layer growing on the substrate surface (q_S). The portion q_A reaches the anode, q_W the chamber walls and the portion q_P is removed from the chamber by the vacuum pump. From this, the following equation is drawn:

$$q = q_T + q_S + q_A + q_R + q_P .$$

The hysteresis effect is caused mainly by reactive gas being adsorbed and desorbed in the coating chamber. Phenomenologically, this effect can be explained as follows: The entire

vacuum vessel with its interior parts (substrate, anodes, chamber walls etc.) acts as a 'gas reservoir' which is constantly filled with or emptied of reactive gas. When the amount of reactive gas admitted is increased, the reservoir must first be filled, before the reactive sputtering process runs in the compound mode. Similarly, when reducing the amount of reactive gas admitted, the reservoir is emptied first, before the sputtering process shifts back to the metallic mode. The delay in returning to the metallic mode is, if also to a lesser degree, supported by the fact that oxide layers must be sputtered from the target first, which advances locally at a different rate for ion-optical reasons (see Chapter 4.2.1.5). It has been shown that the formation of a hysteresis effect depends to a great extent on the sputtering current and less on the simultaneous admission of argon.

Theoretically, hysteresis could be suppressed completely through infinite pump speed of the vacuum pump, but this cannot be realised in practice. The hysteresis effect can be observed when measuring the partial pressure of oxygen in the vacuum chamber and in the stoichiometric analysis of a deposited layer. It can have a significant effect on the properties of the layers.

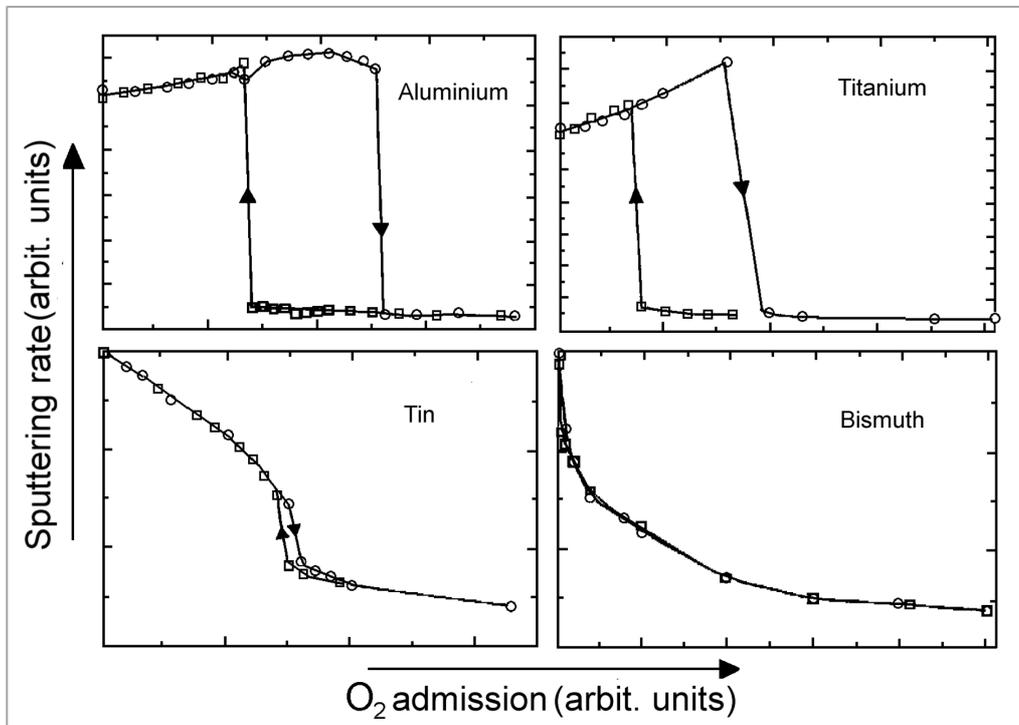


Figure 4.2.1.4.3: Hysteresis effect of several metals for reactive sputtering in an oxygen atmosphere; at increasing \square and decreasing \circ O_2 admission of oxygen

(source: STOLLENWERK)

Figure 4.2.1.4.3 shows the hysteresis effects for reactive sputtering of the metals aluminium, titanium, tin and bismuth with comparable process parameters. From this figure it can be seen that the hysteresis effect is more distinctive with oxides which have a strong affinity to oxygen, such as aluminium oxide (Al_2O_3) or titanium oxide (TiO_2), and less so with oxides which have a weak affinity to oxygen, such as tin oxide (SnO_2) or bismuth oxide (Bi_2O_3). Furthermore, it is also known that bismuth can oxidise in a number of stages, a fact which reduces the hysteresis even more. To summarise, it can be said that the

distinctiveness of the hysteresis effect depends mainly on the oxidising properties of the sputtered material, i.e. its affinity to oxygen and its possible oxidation stages.

From Figure 4.2.1.4.3, it can also be seen that the sputtering rate R_m is in part substantially lower for reactive sputtering than for non-reactive sputtering (compare metallic mode and compound mode). This holds true for reactive sputtering in general and there are several reasons for it. First, it can be caused by the fact that oxides have a higher surface bonding energy than metals. Secondly, it depends on which are the preferred species to be eroded from the target surface. As with hysteresis, here the affinity of the metals to oxygen is also a significant factor. There is a considerable difference, for example, in the sputtering rates of aluminium and titanium in the metallic and in the compound mode, due to their strong affinity to oxygen. Tin and bismuth, however, have a weaker affinity to oxygen and consequently there is little difference between them in terms of sputtering rates. Table 4.2.1.4.1 shows the sputtering rate ratios of metallic and compound mode for some metals used in magnetic field-assisted sputtering (see Chapter 4.2.1.5.2), under comparable conditions.

Metal / Metaloxide	Sputtering rate ratio Metal / Metal oxide
Al / AlO _x	17
Ti / TiO _x	14
Sn / SnO _x	7.8
Bi / BiO _x	7.5

Table 4.2.1.4.1: Sputtering rate ratios of the metallic and compound modes for selected metals (source: STOLLENWERK)

In contrast to the non-reactive sputtering (see Chapter 4.2.1.3), a theoretical interpretation of the reactive sputtering rate must take into account the sticking coefficient, the ion current towards the cathode, the sputtering yield, the mass of the sputtered material and plant-specific parameters. In addition, as has been shown, the reactive sputtering rate also depends on the admission of oxygen q and the interactions during the sputtering process which it induces. Thus the calculation of the reactive sputtering rate appears to be much more complex than the calculation of the non-reactive rate. For this reason, the sputtering rate of reactive processes for individual materials is nowadays determined experimentally, mainly because it is specific to the plant and process concerned. STOLLENWERK has provided the following formula, by means of which the sputtering rates R_m measured can be simulated on the basis of process parameters and a number of known material properties:

STOLLENWERK formula:

$$R_m = \alpha_s F_{O_2} (1 - \Theta_s) m_{O_2} +$$

$$j \frac{(\eta F_{O_2} S_{Me}^{O_2} + F_{Ar} S_{Me}^{Ar})}{(\eta F_{O_2} + F_{Ar})} (1 - \Theta_r) \frac{A_r}{A_s} m_{Me} +$$

$$j \frac{(\eta F_{O_2} S_{Ox}^{O_2} + F_{Ar} S_{Ox}^{Ar})}{(\eta F_{O_2} + F_{Ar})} \Theta_r \frac{A_r}{A_s} (y m_{Me} + D \frac{m_{O_2}}{2})$$

where

j = ion current towards target = $j_{Ar^{++}}, j_{O_2^+}$

α_s = sticking coefficient on substrate surface

$F_{O_2/Ar}$ = particle current density of oxygen/ argon

$Q_{T/S}$ = degree of coverage of target/ substrate + vessel

m_{Me/O_2} = mass of metal/ oxygen

$A_{T/S}$ = surface of target/ substrate + vessel

$S_{Ox,Me}^{Ar}$ = sputtering yield of oxide/ metal due to bombardment with argon ions

$S_{Ox,Me}^{O_2}$ = sputtering yield of oxide/ metal due to bombardment with oxygen ions

η = ionisation ratio Ar/O₂

y = metal proportion of the oxide sputtered off the target (Me_yO_D)

D = oxygen sites per metal atom

This formula is an attempt to interpret the reactions and interactions of reactive sputtering and the differences which occur for individual materials, in order to make the reactive sputtering process comprehensible. The simulation of the hysteresis curves in Figure 4.2.1.4.3 showed, for instance, that for aluminium and titanium the sputtering yield of the metals is higher than that of the corresponding oxides, which causes the different sputtering rates in the metallic and compound modes. For tin and bismuth, these sputtering yield differences are much smaller. With this formula, for instance, the lower sputtering rate of bismuth oxide could be explained by the fact that it is chiefly molecular oxygen rather than bismuth oxide which is sputtered from the target surface.

As mentioned above, without effective control of the gas discharge the different hysteresis effects are also observed in the stoichiometry of deposited layers. The metals with a distinctive hysteresis effect, e.g. aluminium and titanium, shift immediately from the metallic mode to the compound mode, i.e. to the stoichiometrically fully oxidic mode (see Figure 4.1.2.4.3). Tin, with a low hysteresis effect, passes through a transitional stage (SnO) during the shift from the metallic to the stoichiometrically fully oxidic mode (SnO₂). Finally, bismuth, with an almost negligible hysteresis effect, passes through several oxidation stages from the metallic mode to the fully oxidised stage, i.e. the amount of oxygen admitted directly determines the degree of oxidation of the bismuth.

This holds true accordingly for the reactive sputtering of nitrides, carbides and sulphides. From what has been shown in this section, it can be concluded that reactive sputtering is a very complex process which requires a much more rigorous controlling of the process and monitoring of the gas discharge than non-reactive sputtering. Today, it is possible, by means of light emission spectroscopy, to diagnose the light intensity of excited reactively sputtered particles and hence their concentration in the gas discharge zone. On the basis of this diagnosis, it is then possible to control the reactive sputtering. This technique is called plasma emission monitoring (PEM, see also the discussion at the end of Chapter 4.2.1.5.2).

Reactive sputtering in the transition mode leads to higher sputtering rates than in the compound mode, which is particularly economically interesting for materials with a low sputtering rate. However, the sputtering process is generally very unstable in this mode. Nevertheless, by applying very powerful control technology, which simultaneously affects the electric power supply for the gas discharge and the admission of the reactive gas, it is possible to sputter specific metal oxides which have intrinsically low sputtering rates, e.g. SiO_2 and Al_2O_3 , in the transition mode and thus make it economically viable to sputter such oxides.

Figure 4.2.1.4.4 shows the process windows for transition-mode reactive sputtering of some oxide and nitride layers.

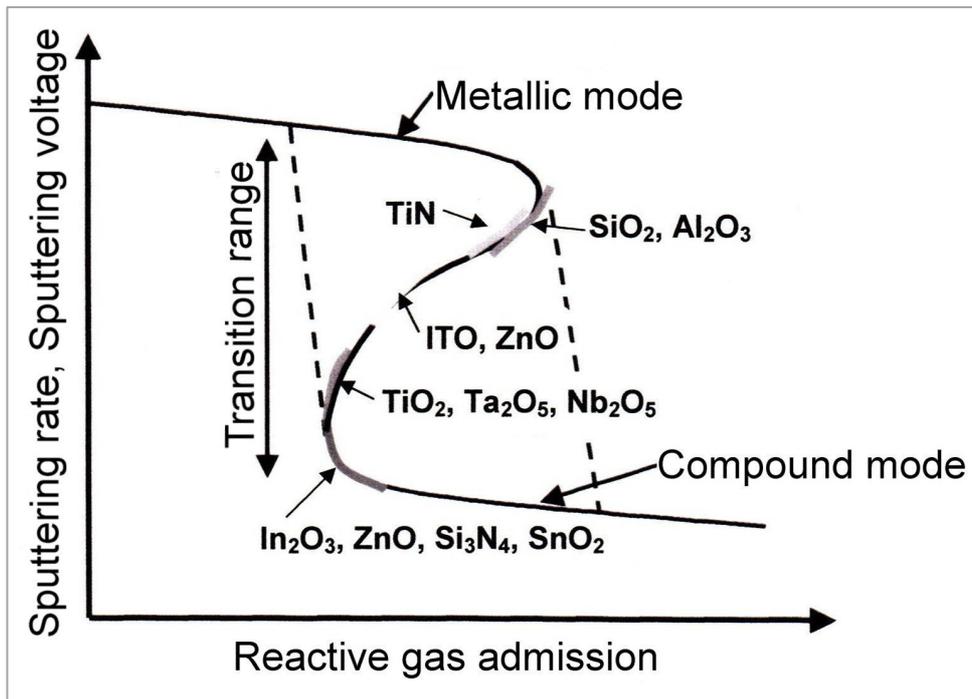


Figure 4.2.1.4.4 Possible process windows for transition-mode reactive sputtering of some oxide and nitride layers used for flat glass coating

Because the bonding between the sputtered materials (e.g. oxides of Bi, Sn, Zn, Ti and Si) and the surface of the flat glass pane is effected by Si-O-Me bridges, metal oxides are generally strongly adhesive on glass surfaces. Furthermore, the layers of these metal oxides grow uniformly from the beginning, because the diffusion rate of the incident particles on the surface is very high. The layers have structures which range from amorphous to polycrystalline, depending on the energy of the incident particles and the substrate temperature.

Generally, it can be said that reactive sputtering is the regular case, because, in practice, the sputtering atmosphere is always polluted by reactive substances (though in small quantities), such as water vapour, oxygen or nitrogen, which desorb from surfaces in the coating chamber, i.e. from the chamber walls, and the substrate as it enters the vacuum chamber. The non-reactive sputtering process described in Chapter 4.2.1.3 is therefore the ideal case which can also be considered as a special case of reactive sputtering.

4.2.1.5 Sputtering techniques

In order to coat large substrates, such as flat glass panes, rod cathodes are used as coating targets. The rod cathodes form a linear source of the material for sputtering and are slightly longer than the panes are wide. The pane is coated by a relative movement of pane and cathode, i.e. either the cathode moves along the fixed pane or the pane moves along the fixed cathode. This technique is called dynamic sputtering as opposed to static sputtering where both cathode and substrate are in a fixed position. However, static sputtering is not suitable for coating large-area substrates. Figure 4.2.1.5.1 shows the principle of dynamic sputtering.

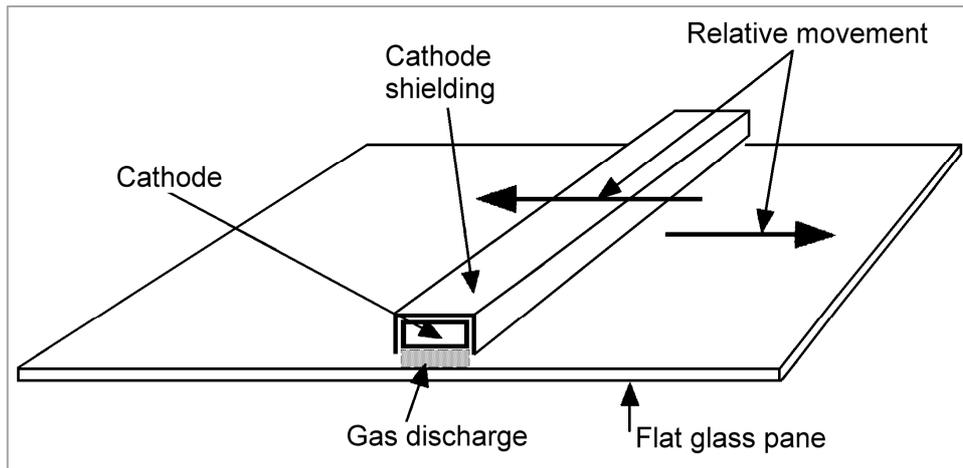


Figure 4.2.1.5.1 Principle of dynamic sputtering

It makes sense to introduce the parameter of a dynamic sputtering rate R_{dyn} for dynamic sputtering processes. R_{dyn} can be defined as the layer thickness in nm which is achieved at a relative movement of cathode and substrate of 1 m/min for a given cathode arrangement and the sputtering conditions. Assuming that the rod cathode surface is planar and the erosion is constant across the entire cathode width b , the following relationship between the static sputtering rate R_{d} as defined in Chapter 4.2.1.3 and the dynamic sputtering rate R_{dyn} applies:

$$R_{\text{dyn}} = R_{\text{d}} \cdot b / v$$

where v is the relative velocity between pane and cathode.

The dynamic sputtering rate is a construction- and process-specific parameter. In order to be able to compare the values established in different coating plants, the sputtering power density (in W/cm^2 cathode surface) should also be given in addition to the specification of the sputtering arrangement. The sputtering rates shown in the literature often do not allow for a comparison of how different systems perform.

The following sputtering techniques have been employed for flat glass coating purposes:

- Conventional DC and AC sputtering
- Magnetic field-assisted DC and AC sputtering, so-called “magnetron sputtering”

where the DC sputtering is carried out with a single rod cathode and the AC sputtering with a dual rod cathode arrangement.

Conventional DC and AC sputtering was used for large-area coating of flat glass only up to the beginning of the 1990's; this type of sputtering could be applied with economically viable sputtering rates only for non-reactive sputtering of the noble metals, gold, silver and copper, and for non-reactive sputtering of bismuth oxide and lead oxide. Due to the higher sputtering rates that could be achieved by magnetron sputtering, and the significantly larger number of materials that could be sputtered economically and in high quality, this technology has gradually replaced conventional sputtering since the beginning of the 1980's. Today, it is the only sputtering technique that is applied for coating flat glass.

Rod cathodes used for coating of jumbo-sized flat glass panes have a length of up to 375 cm. Because the production and handling of targets for cathodes of this length requires special care, an extra section is devoted to this topic (see Chapter 4.2.1.6).

4.2.1.5.1 Conventional DC and AC sputtering

In Figure 4.2.1.5.1.1 as an example, the diagram of a planar rod cathode for conventional sputtering in the DC mode as well as the sputtering behaviour with such a cathode are illustrated.

In this case the cathode consists of a tube with a rectangular cross-section of e.g. 4 cm x 8 cm which has a cooling medium flowing through it. The target is fixed to one side of the tube. The other sides of the tube are shielded with earthed sheet metal so that the gas discharge glows only in front of the target. The cathode is connected to the negative pole of the DC power supply unit; the positive pole is earthed and connected to the shielding and the other interior surfaces of the coating chamber.

Due to the applied sputtering voltage between the target surface and the cathode shielding, an electric field is generated, as shown in Figure 4.2.1.5.1.1.

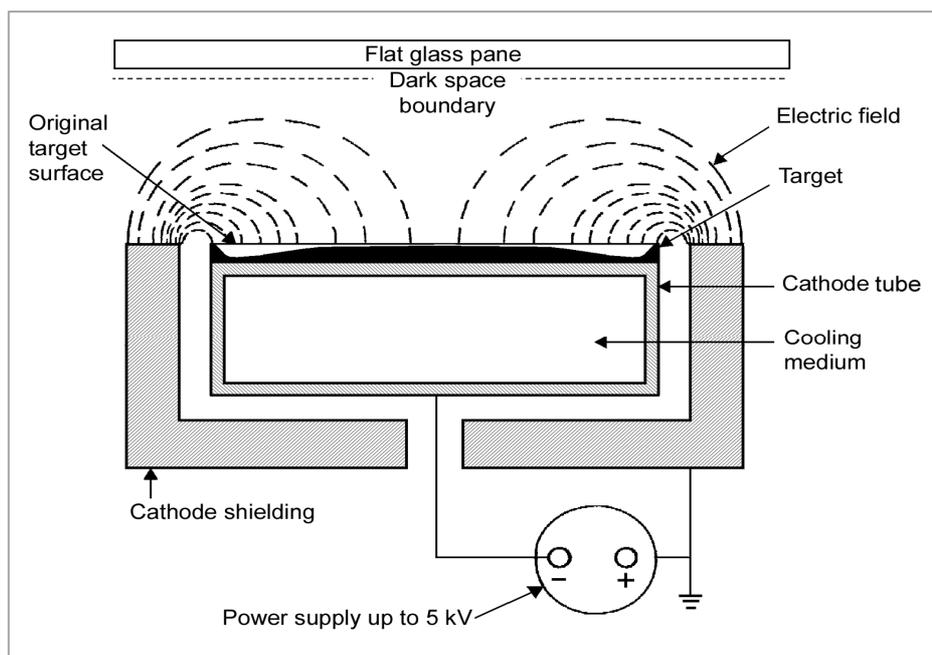


Figure 4.2.1.5.1.1: Design and sputtering behaviour of a planar cathode used for conventional sputtering in the DC mode

This electric field deflects the sputtering gas ions (Ar^+ and O^{2+}) towards the edges of the target so that the target surface is not evenly bombarded. The result is that the erosion and also the sputtering rate is greater along the edges of the cathode surface than at its centre. This is why the target surface gradually becomes larger, requiring in turn that the process parameters (sputtering voltage, gas composition in the case of reactive sputtering and/or the velocity of the relative movement between target and pane) must be constantly readjusted, as the target erosion proceeds. This topic will be dealt with in more detail in Chapter 4.2.1.7.

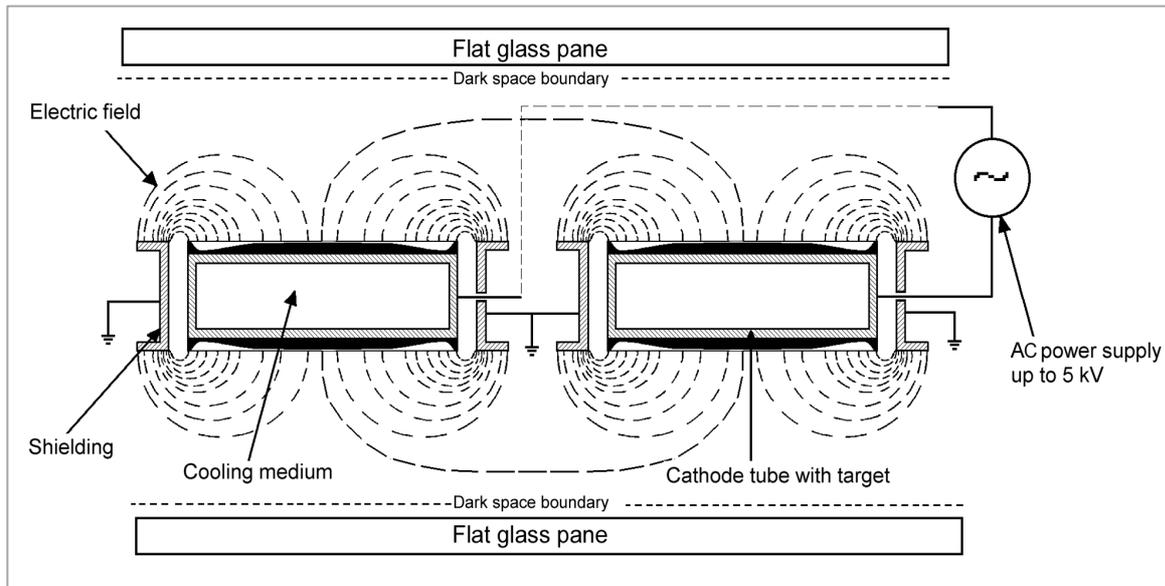


Figure 4.2.1.5.1.2: Design and sputtering behaviour of planar cathodes used for conventional sputtering in the AC mode

The arrangement needed for conventional sputtering in the AC mode differs somewhat from that in DC mode. As shown in Figure 4.2.1.5.1.2, two cathodes are installed in a parallel arrangement. Again, both have a cooling medium flowing through them.

Both wide sides of the cathodes can have a target attached to them, so that two panes can be coated simultaneously. The sides of the cathodes which do not carry a target are shielded with sheet metal. This shielding is also earthed and can be used simultaneously as a holding apparatus for the cathode tubes. An AC voltage is supplied to both cathodes so that, during each half-wave, one of the cathodes sputters while the other acts as the anode. The polarisation alternates according to the frequency of the voltage.

AC sputtering with the dual cathode arrangement has a number of advantages. First, since the discharge process is interrupted for a short time while the voltage wave passes the zero point, the unwanted arc discharge can thus be suppressed. Secondly, the problems experienced in conjunction with the disappearing anode effect in reactive processes (see above) do not occur either. When industrial-scale flat glass coating by means of sputtering first began in the early 1960s, this dual cathode arrangement was employed so that an unregulated 50 Hz AC voltage was connected to the cathodes by an ordinary high voltage transformer. When the demand for uniform and reproducible layers increased, sputtering in the AC mode was abandoned because of the lack of suitable voltage-regulating power supply units at that time. As regulated DC power supply units had been available for a long time, DC sputtering gained importance. The dual cathode arrangement has been

rediscovered in connection with magnetron sputtering for flat glass coating (see Chapter 4.2.1.5.2).

Conventional sputtering processes are carried out at a pressure of $p = 10^{-2}$ to 10^{-1} mbar. The panes are positioned 30 to 60 mm in front of the cathode, behind the boundary of the dark space. Because scattering of the sputtered particles in the sputtering gas atmosphere is very high, the distance between pane and dark space boundary should be kept to a minimum so that as a high as possible sputtering rate can be achieved. For the same reason the distance between pane and cathode must be precisely adjusted, in order to maintain an uneven layer thickness across the entire large-area surface of the pane. Coating large-area panes by conventional sputtering consequently requires considerable attention to be paid to the adjustment of the holding and conveying apparatus for cathodes and panes.

A major problem experienced when coating large-area flat glass panes by means of conventional sputtering is the uneven heating of panes, caused by incident electrons as explained in Chapter 4.2.1.3. Temperature differences of up to 40 K can occur within a pane, which may lead to warping of the pane and, because a constant distance to the cathode is then not maintained, resulting in an uneven layer thickness. For this reason reactive sputtering can only be run at reduced power, because, particularly in reactive processes, a large number of electrons are released at the target, as explained in Chapter 4.2.1.4.

The sputtering power density for conventional sputtering is approximately 5 W/cm^2 target surface. Only about 25 % of the energy which reaches the target surface by the impulse transfer of the sputtering gas ions is utilised for the erosion of the target material. The remaining 75 % is transformed into heat, which must be removed from the system by the cooling medium so that the target and the cathode do not become overheated. Because of the high sputtering voltage ($U_A > 2 \text{ kV}$) applied in this case, transformer oil is usually used as a cooling medium. It is possible to use water instead, but this makes the electrical insulation much more complex.

As mentioned above, the sputtering rate for conventional sputtering is generally quite low so that only a few materials can be sputtered economically on an industrial scale. Gold, silver, copper, bismuth oxide and lead oxide are among them. The dynamic sputtering rate R_{dyn} of these materials for conventional sputtering is about 10 nm at a relative movement of 1 m/min and under the usually applied conditions. All the other materials commonly employed today for flat glass coating have noticeably lower dynamic sputtering rates and are therefore not economically viable for conational sputtering.

4.2.1.5.2 Magnetron sputtering

Cathode design and configuration

Figure 4.2.1.5.2.1 shows the general design of planar magnetron cathodes used for large area flat-glass coating with magnetron DC sputtering today. Again, the target consists essentially of a pipe of rectangular cross-section. Behind the target, a series of permanent magnets is configured to generate a magnetic field in front of the target with the magnetic field lines running as illustrated. The magnetic field strength is a few hundredths of a Tesla.

The cathode body is made of anti-magnetic material, so that it does not influence the magnetic field. The three non-active sides of the cathode are also shielded by anti-magnetic material. The negative pole of the DC power supply is connected to the cathode; the positive pole is connected to the anode and is earthed, as are the walls of the sputtering chamber

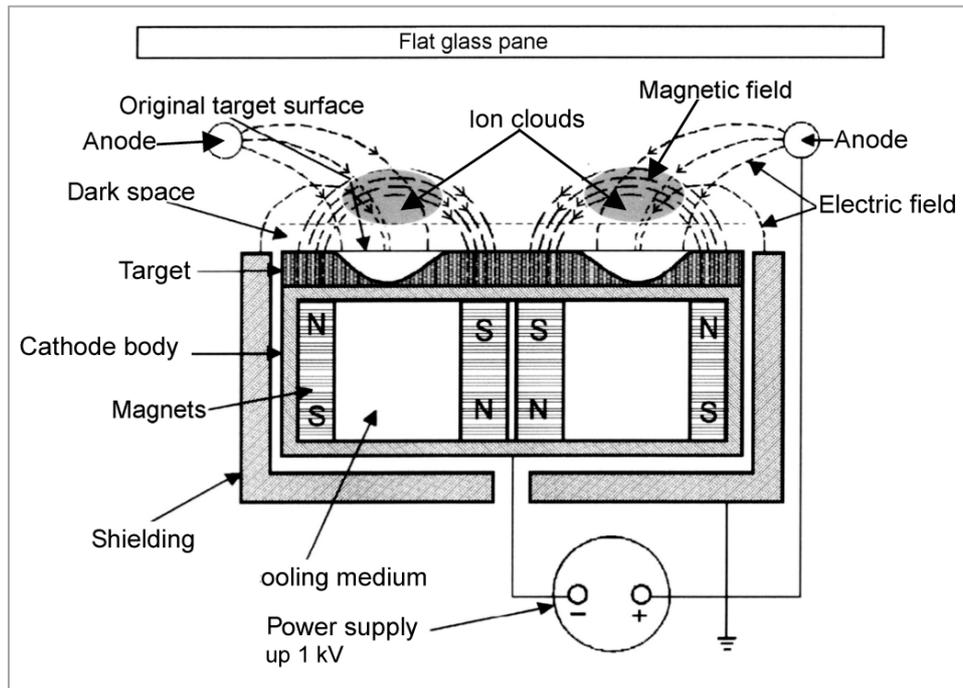


Figure 4.2.1.5.2.1 Design and sputtering behaviour of a planar magnetron rod cathode in the DC mode

The sputtering process using such magnetron cathodes is normally run in a pressure range of 10^{-2} to 10^{-3} mbar, i.e. the pressure range is an order of magnitude smaller than for conventional sputtering. At these pressures, the sputtered species collide much less frequently with the sputtering gas atoms along the path to the substrate than for conventional sputtering, so that deceleration is greatly reduced and the spacing between the target and the substrate pane can be up to 30 cm for magnetron sputtering. In general, a distance of 60 mm to 150 mm is chosen. The longer distance between the cathode and the substrate compared to conventional sputtering means that the alignment tolerance for the pane distance is significantly higher, such that even slightly curved panes can be coated by magnetron sputtering.

The LORENTZ force deflects electrons released from the target surface at right angles to the intersecting electric and magnetic fields and, as shown in Figure 4.2.1.5.2.2, they move on cycloidal paths along the target surface just like on a 'racetrack'.

This prolongs the course of the electrons, which leads to amplified collision ionisation, called the PENNING effect, whereby the ionisation degree of the sputtering gas is increased significantly compared to conventional sputtering, despite the lower sputtering pressure used in magnetron sputtering. Owing to this effect, ion clouds are formed close to the target, in particular where the fields intersect almost at right angles and where the deflection of the electrons is greatest, because the LORENTZ force is at its maximum here. Compared with conventional sputtering, the significantly higher sputtering gas ion density and a very

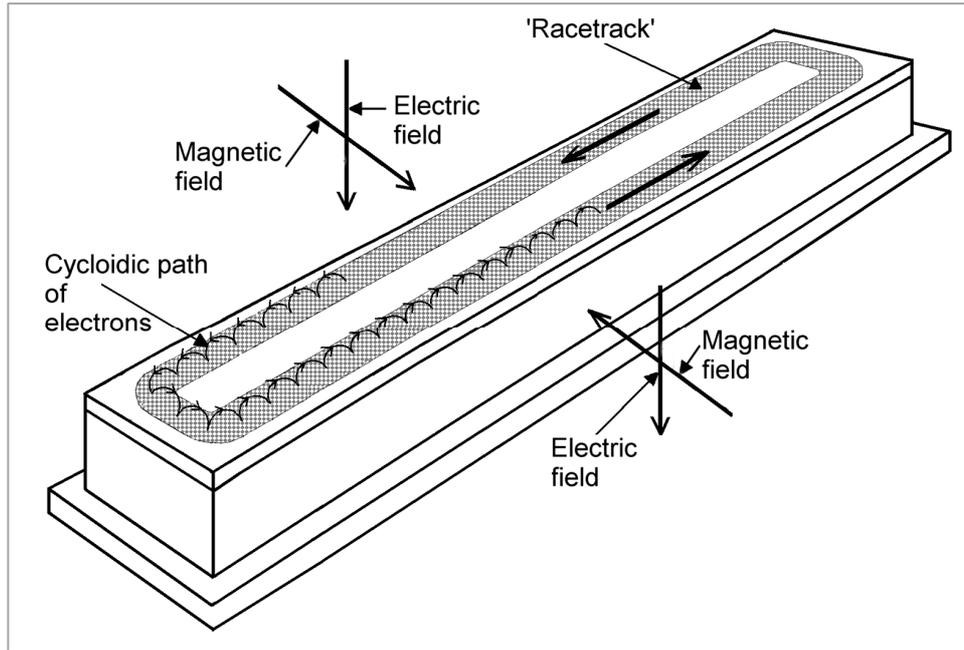


Figure 4.2.1.5.2.2: Magnetron sputtering: electron paths

intensive plasma discharge close to the target lead to the following features of magnetron sputtering:

- The dark space D is only a few millimetres wide (see Figure 4.2.1.2.1). Thus, it is a factor of ten smaller than in the conventional sputtering process
- The current density j of the sputtering ions to the cathode and thus the sputtering current are considerably higher
- The sputtering voltage U_B is only 200 to 1,000 V
- The sputtering power density may be up to 15 W/cm^2 , about 75 % of which is transformed into heat and must be removed again from the system
- The sputtering rates R_d and R_{dyn} are a factor of ten higher

It should be noted that the sputtering gas ions are hardly deflected at all by the interaction between the magnetic and electric fields, as their mass is much higher than an electron mass.

The high sputtering rate and the resulting broad range of application possibilities are the properties which make magnetron sputtering so interesting for coating purposes. Magnetron sputtering boasts the additional advantage that the electrons decelerated by the collisions along their course are sucked towards the anodes, so that – in contrast to the conventional sputtering process – only very few impact on the glass substrate with their full energy. As a result, the substrate is not heated up and remains close to room temperature. Thus, this technology also allows temperature-sensitive substrates to be coated. Also, warping of large-area glass panes during coating is negligible, avoiding the associated problems encountered in conventional sputtering.

However, a disadvantage of planar magnetron cathodes is that sputter erosion is very inhomogeneous across the target width (see Figure 4.2.1.5.2.1). This is related to the fact that the electron deflection is strongest and the sputtering gas ionisation is greatest where

the magnetic field runs parallel to the cathode surface. Thus, target material is eroded preferentially along two parallel grooves along the length of the planar magnetron cathodes. The target yield from the planar magnetron cathodes currently used is thus only about 25 %. Because the target surface area increases as the erosion progresses, sputtering parameters must be constantly readjusted to maintain a constant sputtering rate (see Figure 4.2.1.5.3.1).

To achieve an even coating it is necessary that the magnetic field strength along the cathode is kept as constant as possible. For this reason the individual magnets of the cathode have to be matched carefully according to their field strength. Apart from limiting the tolerances on the field strength of individual magnets during magnet selection, this is done by adapting the field strength of individual magnets by means of iron sheets, so-called shunts, with which the magnet poles are covered. The variation in the magnetic field strength should be less than 1 %. Experience has shown that it is useful to adapt the magnetic field strength according to the sputtering material used. Cathodes for sputtering materials with a lower sputtering yield S can be equipped with stronger magnetic fields than those for materials with higher sputtering yields.

Figure 4.2.1.5.2.3 shows a planar magnetron cathode as used for flat glass coating. It can be seen clearly that the target is eroded along a “race track” mainly below the ion cloud, which is typical for magnetron sputtering with such a cathode.



Figure 4.2.1.5.2.3:
Planar Magnetron cathode for flat
glass coating, length 3.75 metres
(source: VON ARDENNE
ANLAGENTECHNIK DRESDEN, Germany)

Nowadays, for improving the thickness uniformity of coatings the magnet assembly of magnetron cathodes is divided along the cathode length in segments which can be separately motor-driven shifted parallel to the target. This works as follows: Shifting a magnet segment in direction to the target increases the magnetic field in front of the target area of this segment and thus also the sputtering rate and vice versa. Each motor is separately shiftable from outside of the coating plant. This technique is combined with optical measurements of thickness deviations - i.e. lacking uniformity - during the coating process. Thus, because today panes are normally transported below the cathodes during the coating

process (see Figure 4.2.1.5.1) the lacking uniformity of coating thickness can be adjusted in strips in the direction of transportation of panes by actuating the motor of the appropriate segment or segments. In the case of multi-layer systems, each partial layer system can be adjusted during the coating process in the same manner. This technique is applied for high-tech solar-control coatings and anti-reflection coatings with up to 7 individual layers (see Chapter 5.2 and 5.3, Part II) with in-line sputtering plants (see Figure 4.2.1.7.2.1) marketed today for which a thickness uniformity of each individual layer of $\pm 1\%$ is required. This technique was also transferred in an adapted manner to rotatable rod-shaped magnetrons whose design is depicted in Figure 4.2.1.5.2.4.

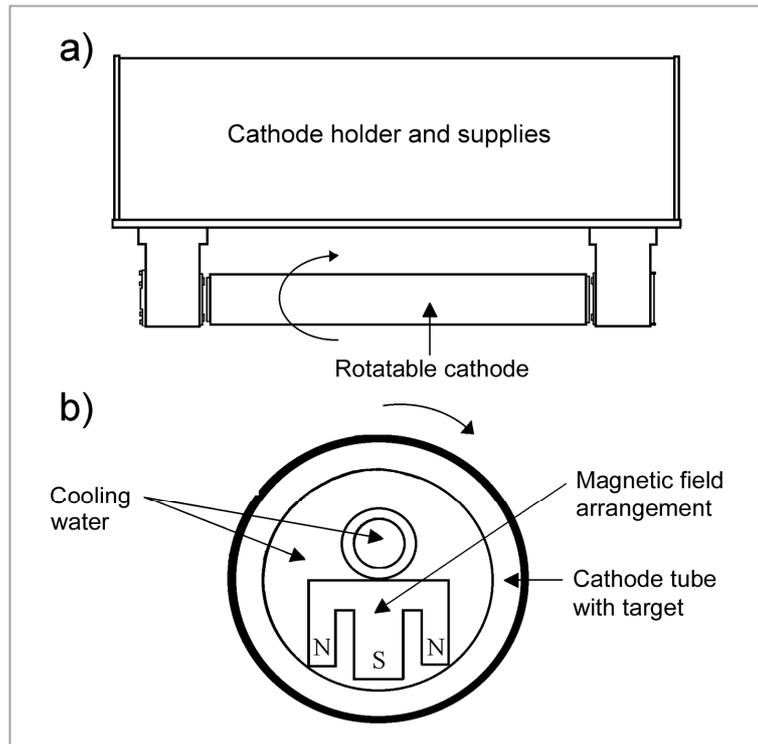


Figure 4.2.1.5.2.4:
Diagram of a rotatable magnetron cathode
a) side view b) cross-section
(source: AIRCO COATING)

In addition to planar magnetron cathodes, rotatable rod-shaped magnetron cathodes are also used for coating large-area flat glass. The magnets are arranged in a tube of annular section, which rotates continuously around the magnets together with the target attached to its outer wall during the sputtering process. Because of the rotary movement, however, the target is eroded evenly. This cathode design has the advantage that the target yield is much higher than that for planar magnetron cathodes. Figure 4.2.1.5.2.4 shows the general design of a rotatable magnetron cathode.

However, the disadvantage of rotatable magnetron cathodes is the difficulty and high cost of producing tube-shaped targets compared to planar magnetron cathodes.

A major problem of magnetron sputtering is arcing (occurrence of sporadic arc discharges), as mentioned above, which can damage or even destroy the deposited coating and also the target. There are various reasons for arcing. One cause is larger or smaller particles, which fall off the target, the cathode, the anode or the wall around the cathode and enter the gas discharge zone, where they are charged. They are then accelerated along the "race track", evaporate and thus cause a gas discharge, which may have catastrophic results.

Another reason for arcing is the high electric field strength across the dark space due to the small width of the dark space in magnetron sputtering. The electric field strength E of the dark space can be expressed as

$$E \sim U_A/D$$

where U_A is the sputtering voltage (see Figure 4.2.1.2.1) and D is the width of the dark space. As a result, the danger of peak discharge is high despite the low sputtering voltage, due e.g. to 'hillocks' or 'spikes' caused by irregular erosion in the sputtering groove of the target that create a high local electric field strength and initiate an arc discharge.

In reactive sputtering, another main reason for arcing is the re-deposition of electrically insulating sputtering materials, e.g. oxides and nitrides, on the target, as already discussed in Chapter 4.2.1.4. Electrically insulating coatings are formed on the target outside the erosion zone (see Figure 4.2.1.5.2.5). Positively charged sputtering ions which arrive on the surface of these coatings are neutralised, so that the potential on this surface drifts toward 0 V, so that in the end the entire sputtering voltage U_A can drop across this re-deposited coating.

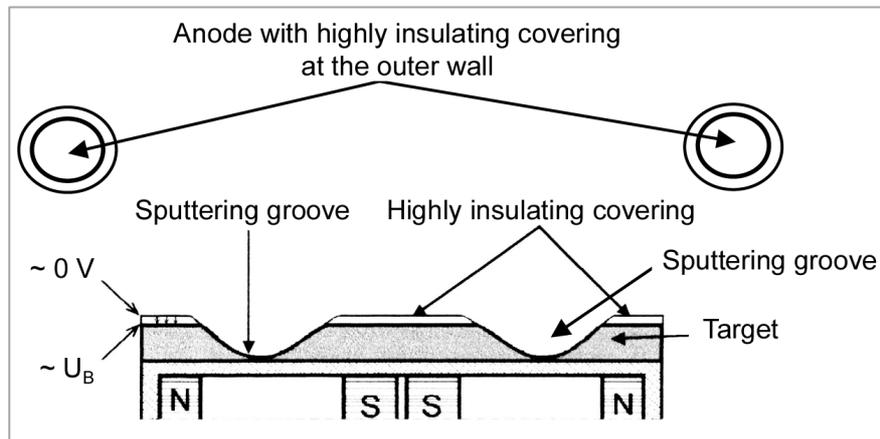


Fig. 4.2.1.5.2.5: Insulating coverings on the target and anodes in reactive sputtering processes

As this coating is very thin (thickness d), again the electric field U_A/d may become strong enough to cause electrical breakdown and then arcing via evaporated or dislodged material. It has been observed that arcing caused by this mechanism increases with the electrical resistance of the re-deposited layers. This explains why highly insulating materials such as SiO_2 or Al_2O_3 can practically not be coated by DC magnetron sputtering.

As already mentioned in Chapter 4.2.1.4, arcing can be reduced by electronic measures in the power supplies (see below) by interrupting the sputtering process briefly if arcing occurs. In doing so, it is essential to recognise arc formation in its initial stages. A further option to avoid arcing is to sputter with low sputtering voltages, but this also means a low sputtering rate, resulting in lower economic viability of the sputtering process. Arcing, particularly that is due to re-deposition of electrically insulating materials on the target surface, can also be suppressed by applying a positive voltage briefly to the magnetron cathode, so that the surface of the re-deposited coating is negatively electrically charged by the incident electrons. This is done with specially adapted power supplies and is called "pulse sputtering".

A further disadvantage of reactive sputtering processes with DC magnetron cathodes is that the anodes arranged at the sides are also progressively covered with insulating material, so that the resistance in the electric circuit increases and the electric potential conditions change during the sputtering process (see Chapter 4.2.1.4). This effect is also known as the 'disappearing anode effect'. The changing electric potential conditions can detrimentally affect the homogeneity of the sputtered coating and its physical properties, e.g. refractive index.

The problems of arcing, particularly due to re-deposited material, and the disappearing anode effect are solved by a dual cathode arrangement and an alternating current (AC), so-called AC magnetron sputtering, which has to become standard practice today. Figure 4.2.1.5.2.6 illustrates the design of such an AC planar magnetron configuration.

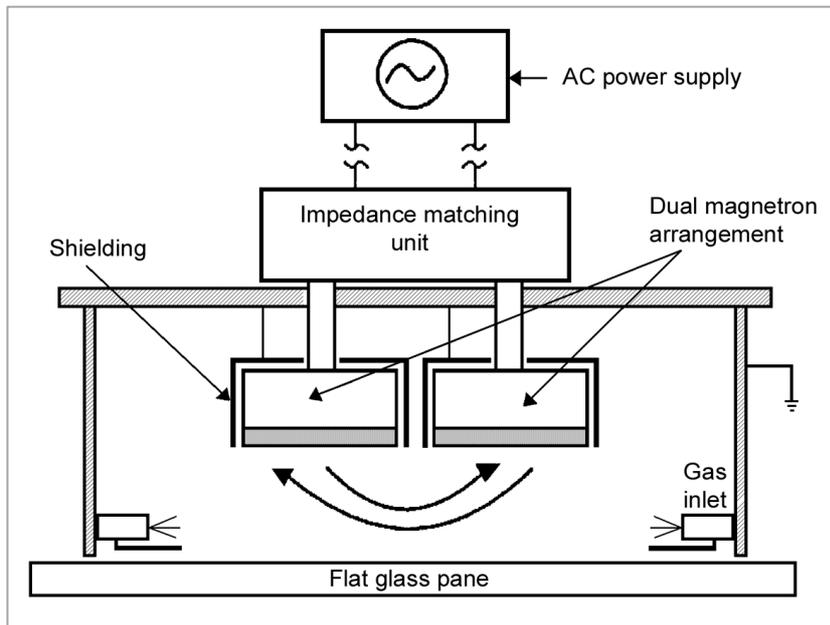


Figure 4.2.1.5.2.6: Design of a dual planar magnetron sputtering arrangement

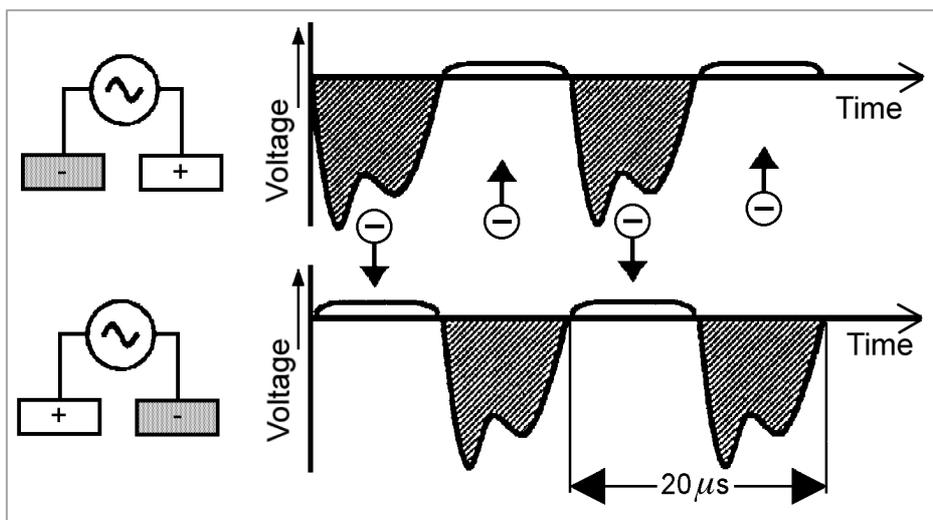


Figure 4.2.1.5.2.7 Change of cathode potential with time in an AC magnetron configuration

As for conventional AC sputtering (see Chapter 4.2.1.5.1), now two magnetron cathodes designed similar to that shown in Figure 4.2.1.5.2.1 are arranged in parallel. The gas discharge is excited by AC voltage at a frequency in the range from 20 to 100 kHz, i.e. at medium frequency (MF), which is applied by an AC power supply via an impedance adapter to the cathodes. As in conventional AC sputtering (see Figure 4.2.1.5.1.2), the AC voltage causes negative potential to be applied to one electrode and positive potential to the other for sputtering during one half-wave, and then the polarities are reversed during the second half-wave, so that each electrode alternately functions as an anode and a cathode. In this way, there is no need for a separate anode with all the difficulties it causes. AC magnetron sputtering can also be operated with rotatable magnetron cathodes arranged in parallel. Figure 4.2.1.5.2.7 shows the change of potential with time for AC magnetron cathodes operation.

Figure 4.2.1.5.2.8 shows photos of different AC magnetron configurations, also called 'dual magnetron arrangement'.

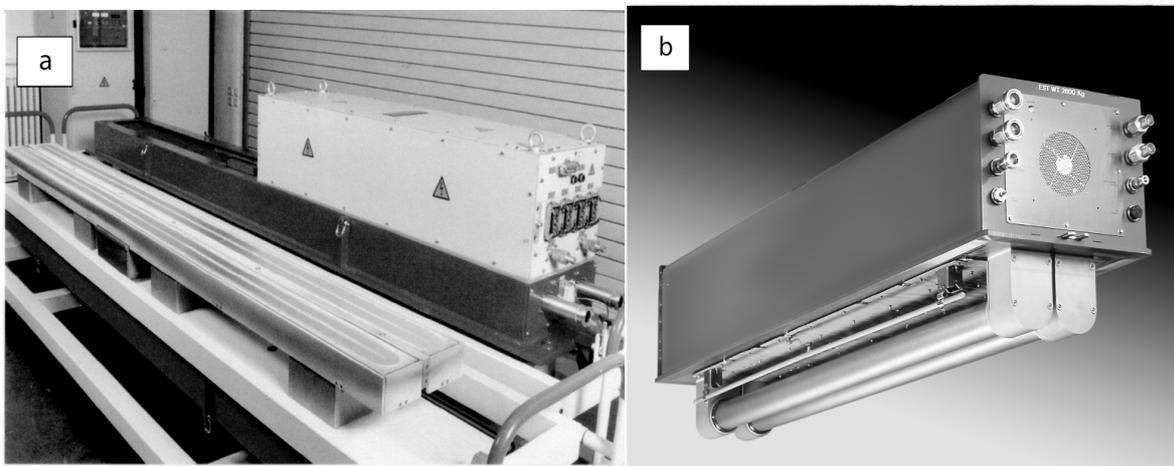


Figure 4.2.1.5.2.8 Applied AC magnetron configurations

a) with planar cathodes b) with rotatable cathodes

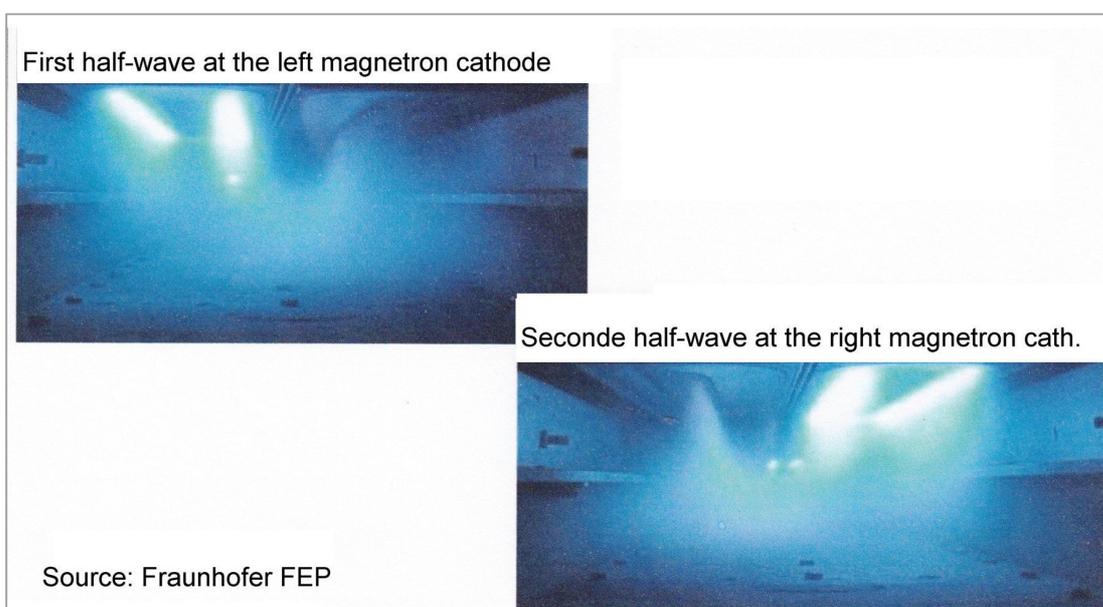


Figure 4.2.1.5.2.9 High-speed images of the ion clouds from the two voltage half-waves in a planar magnetron arrangement.

(source: Fraunhofer FEP, Dresden GERMANY))

Figure 4.2.1.5.2.9 shows high-speed images of the ion clouds from the two voltage half-waves in a planar magnetron arrangement. It can be seen clearly that the ion cloud moves from one cathode to the other and back again during one sputtering period. AC magnetron sputtering has the major advantage for reactive sputtering processes that both the disappearing anode effect and arcing can be suppressed, i.e. a very stable gas discharge is maintained for very long periods of time. However, AC magnetron sputtering does not offer any advantages for metallic sputtering.

Types of gas discharge excitement

The gas discharge for sputtering is excited by power supplies and can apply various different procedures. Figure 4.2.1.5.2.10 shows the voltage-time curves for types of gas discharge excitement possible today for sputtering processes with *one* cathode, regardless of whether it is a planar or rotatable type. A distinction is made between DC mode with continuously fed direct voltage and unipolar and bipolar pulse mode. Unipolar pulse mode means that the cathode is fed a pulsed square wave voltage at a given frequency, whereby the ratio of the on and off phase may be varied. In the bipolar pulse mode, the potential is reversed in the off phase, so that a charge reversal of the target surface takes place, just as in the dual magnetron cathode arrangement. The ratio between 'on' phase t_2 and 'on plus off' phase t_1 is also referred to as a 'duty cycle'.

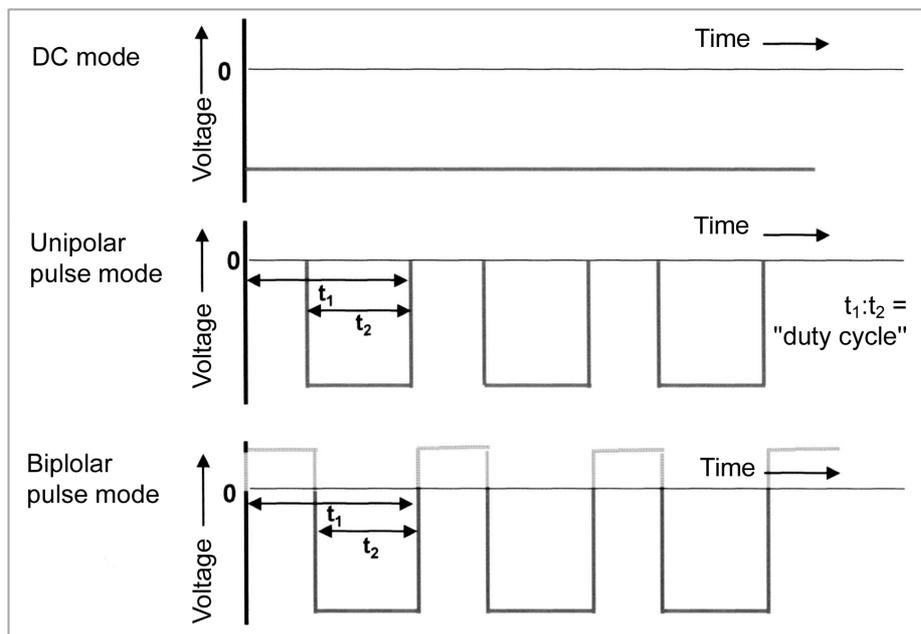


Figure 4.2.1.5.2.10: Types of gas discharge excitement for sputtering with one magnetron cathode

Figure 4.2.1.5.2.11a shows the voltage-time curve for sinusoidal excitement of the gas discharge in a dual magnetron cathode arrangement, which are again identical for planar and rotatable type. During the negative half-wave, i.e. while one of the cathodes is sputtering, the surface of the other cathode is fed positive potential and the electric potential of the covering areas reverses due to electron bombardment and vice versa. The excitement frequencies are in the MF range, i.e. between 10 and 100 MHz. Today, the gas

discharge of the dual magnetron arrangements is also excited in a pulsed instead of a sinusoidal manner. Figure 4.2.1.5.2.11b shows the voltage-time curve for such a case. During the negative phase of one cathode, the other one is fed positive voltage. The difference from case a) is that a defined duty cycle ratio can be set in the two voltage phases through the pulse mode, which allows the layer properties to be influenced, for example. Pulse sputtering may result in a higher sputtering performance compared with sinusoidal excitement which, in the case of reactive TiO_2 sputtering for instance, allows the deposition of the rutile phase with the desired high optical refractive index. Pulse sputtering also requires excitement frequencies in the range of 10 to 100 MHz. The decision regarding the optimal type of excitement depends on the material to be sputtered and on the desired layer properties and requires experience.

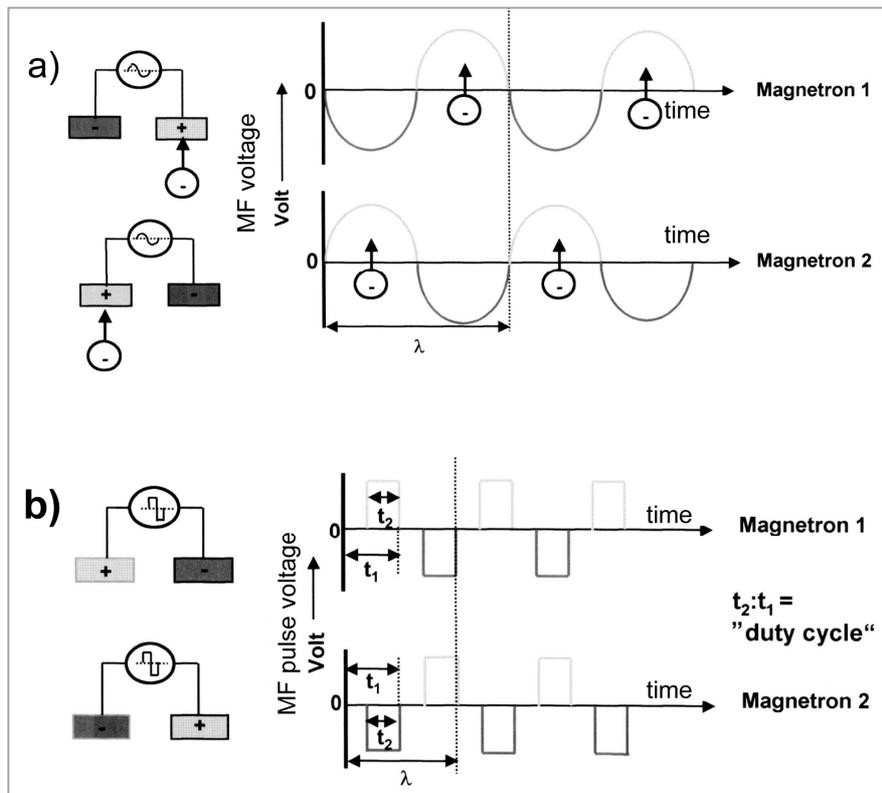


Fig. 4.2.1.5.2.11: Types of gas discharge excitement for sputtering with a dual magnetron cathode arrangement:
 a) sinusoidal excitement, b) pulse excitement

Power supply units for sputtering processes

The requirements for a modern power supply unit for magnetron sputtering include the option to select the different methods of exciting the gas discharge discussed above, current, voltage and power control modes and sophisticated arc management, i.e. circuits which prevent the transition from normal glow discharge to destructive arc discharge. As discussed above, there may be several reasons for arcing. An arc management system aims to detect electronically an arc discharge when it is in a nascent state and to decide how it can be suppressed automatically. If the arc discharge is so powerful that it cannot be suppressed, it must be blanked by a brief interruption in the power supply to prevent major

damage. Most arc management systems also incorporate a burn-in routine, i.e. a slow gradual increase of the sputtering voltage for new targets, the surface of which may be contaminated with impurities or loose particles from manufacturing or installation, which may also lead to arcing.

Gas admission

As there are growing demands on the coatings, e.g. as regards colour uniformity, i.e. evenness of layer thickness across the entire coated glass surface, the admission of the sputtering gas is of particular importance.

For metallic sputtering processes, e.g. in a pure argon atmosphere, a single pipe gas distribution system will usually suffice (see Figure 4.2.1.5.2.12a), where the quantity of gas delivered through the gas nozzles in the distributor pipe decreases from the inlet into the distributor pipe towards its end because of the different flow resistance. However, this has no impact on the coating. For reactive sputtering processes, a binary distribution system becomes necessary, as shown in Figure 4.2.1.5.2.12b, where the flow resistance to the sputtering gases is identical at each nozzle, so that the entire length of the cathode is provided with even gas composition and quantity. The gas distributor pipes are arranged directly along the cathodes, on either one or both sides of the cathodes.

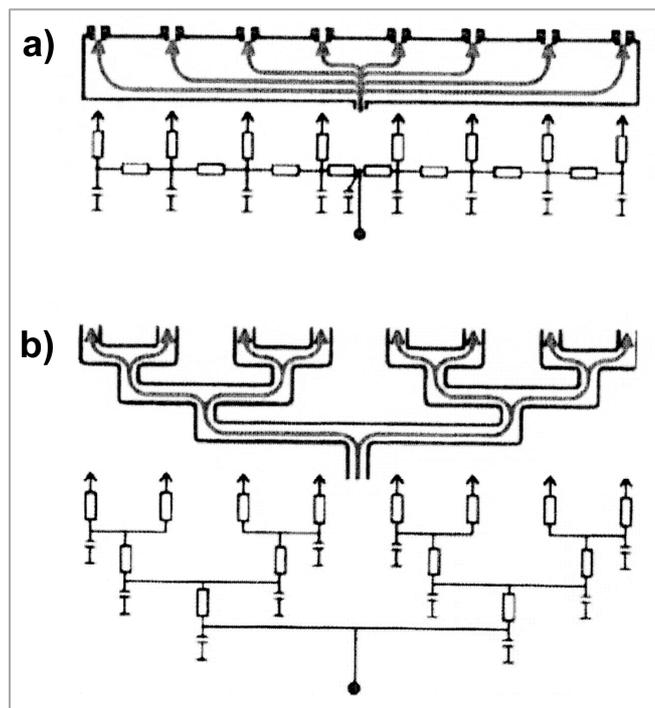


Fig. 4.2.1.5.2.12:
Sputtering gas distribution
systems:
a) single pipe distribution,
b) binary distribution
system

Gas discharge control

Gas discharge control has also become a crucial process parameter. Metallic sputtering processes only require the electrical parameters, current, voltage or power, to be controlled depending on the coating material, which can alternatively be done with modern power

supply devices. By contrast, for reactive sputtering processes to be economically viable, they must be run in the transition mode between the metallic and compound modes, i.e. operation at Point A in Fig. 4.2.1.4.1. To achieve this, the gas composition, e.g. the argon/oxygen or argon/nitrogen ratio, must be controlled at the same time as the voltage is maintained at the pre-defined value U_A . Reliable deposition e.g. of a fully oxidised coating at or near operating point A can be achieved by analysing the oxygen partial pressure in the gas discharge by using a lambda probe, as is also applied in cars, and controlling the gas admission. More exact control of the complete composition of the sputtering gas can be implemented by analysing the emission spectrum of the gas discharge. This analytical method is also called 'plasma emission monitoring' (PEM) (see also explanations in Chapter 4.2.1.4). It is based on the phenomenon that the admitted sputter gas species collide with the sputtered species in the gas discharge zone so that these species are excited and emit light. The sputtering rate will be constant if the ratio of the sputtered species excited by the collision with the admitted reactive sputtering gas to the reactive gas admission is constant. Therefore, the basis of the PEM technique is to measure and control the intensity of a typical signal of the emitted light of the sputtered species in dependence on the reactive gas admission. I.e. this light signal is proportional to the sputtering rate of the sputtered target material. Figure 4.2.1.5.2.13 shows the design of a control circuit using PEM for reactive sputtering of metal oxide or nitride in combination with the AC magnetron technique.

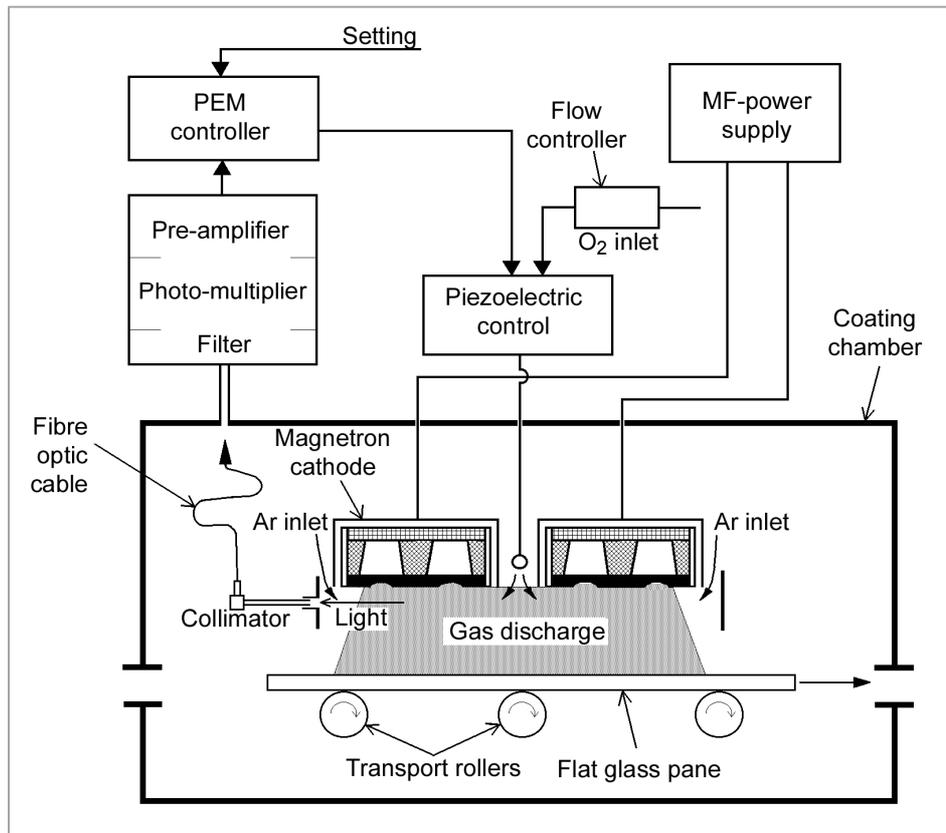


Figure 4.2.1.5.2.13: Diagram of a PEM control circuit for the stabilisation of the reactive sputtering process using the AC magnetron technique

(source: VON ARDENNE ANLAGENTECHNIK DRESDEN, Germany)

The light emitted by the gas discharged is collimated and then transmitted by optical fibres to a filter which separates a typical light signal that depends on the material to be sputtered. The intensity of the typical light signal is converted in a photomultiplier to an electric signal and subsequently amplified. The PEM controller compares the input signal with the set value and uses the difference to determine the admission rate of the reactive gas with a piezoelectric control valve. When the cathodes are as long as are typical for flat-glass coating, the emission spectrum from the gas discharge can be monitored at several positions distributed along the length of the cathode. The control circuit with a lambda probe is arranged analogously. However, this analytical method can be used only to measure and control the reactive sputtering with oxygen, but it is less expensive than the controlling with PEM.

Sputtering rates

The sputtering rates for metals deposited in magnetron sputtering processes are always high enough for all today's applied coatings on large-area flat glass. However, certain control measures may be necessary with several reactively sputtered materials to ensure the economic viability of the process (see Figure 4.2.1.4.4)). Table 4.2.1.5.2.1 shows the sputtering rates in different process conditions for several materials which are difficult to sputter in the reactive mode. From Table 4.2.1.5.2.1, it is evident that the sputtering rates achieved with AC magnetron sputtering are sometimes appreciably higher than those for DC magnetron sputtering. It has been reported that materials such as SiO_2 , Si_3N_4 , TiO_2 and Al_2O_3 , which are otherwise difficult to sputter, can be deposited as coatings onto large-area flat glass by AC magnetron sputtering at adequate sputtering rates and with practically no arcing. When TiO_2 is deposited by AC magnetron sputtering, the technically very interesting rutile structure can be formed due to the high energy of the positive ions impacting on the coating during the sputtering process.

Coating	AC-Sputtering rate R_{dyn}^* (nm) at $v = 1 \text{ m/min}$	Refractive index n	R_{dyn} for AC / R_{dyn} for DC
SiO_2	55	1.47	6
Si_3N_4	35	2.05	-
TiO_2	22	2.6 (rutile)	5
Ta_2O_5	80	2.18	2
SnO_2	80	2.0	2.5
ZnO_2	70	2.0	3
Al_2O_3	35	1.65	-

* R_{dyn} for power densities of 10 to 12 W/cm^2

Table 4.2.1.5.2.1: Dynamic sputtering rates R_{dyn} of reactively sputtered materials

(source: VON ARDENNE ANLAGENTECHNIK DRESDEN, Germany)

A further advantage of reactive sputtering with the AC magnetron technique for some materials can be the property that the substrate can reach a negative potential of up to 200

V due to the positive phases of the cathode. This causes the coating to be bombarded intensively during the sputtering process by positive ions, e.g. Ar^+ ions, which can lead to a higher degree of crystallinity in the coating compared to that produced by DC sputtering. This in turn can affect the coating properties positively. In addition, the generally more stable gas discharge in AC magnetron sputtering means that significantly higher electrical power density can be applied for sputtering, i.e. much higher sputtering rates are possible, which is particularly advantageous for oxide or nitride materials that are sputtered reactively. However, this is possible only if the melting point of the target material permits this, as most of the electrical energy that is introduced for the sputtering process is converted into heat in the target (see above).

The following information on equipment design is also important: AC magnetron sputtering demands that the two parallel cathodes have very uniform magnetic fields. As the magnetic fields of the two neighbouring cathodes overlap, less uniform magnetic fields or cathodes with non-parallel alignment results in variable sputtering rates along the cathode length and thus to uneven coatings. In addition, because high-frequency harmonics occur during the sputtering process due to the non-linear characteristic of the gas discharge (see explanation relating to Figure 4.2.1.2.1), the AC magnetron cathode arrangements must be well shielded against emission of high-frequency waves to prevent disturbing interferences with the surroundings. This concerns as well neighbouring cathodes as exterior electronic equipments as the radio traffic in general.

4.2.1.6 Targets for flat glass coating and their production

In Chapter 4.2.1.2 it has already been explained that the coating material is attached to the cathode body in the form of a metal bar and is called the target.

Apart from the process control mechanisms, the quality of the target has a major effect on the properties of the deposited layer and thereby on its functionality, but also affects the sputtering rate and target life and consequently the economic viability of the sputtering process. As explained in the previous chapters, targets with a length of up to 3.75 m and a width of up to 0.25 m are used for sputtering, so that the total target surface amounts to about 1 m².

In order to provide the required properties of the layer throughout the entire lifespan of the target, it is important to ensure that the target material has adequate purity, a uniformly high density, a uniformly fine-crystalline structure and, in the case of alloys, an even distribution of the components. A target purity of 99.9 % is considered adequate for most flat glass sputter deposition applications. However, in the case of sputtering layers with semi-conductive properties, the level of impurity allowed is measured in ppm (1 ppm means one impurity atom per one million atoms). A uniformly high density of the target material is essential to avoid arcing, because with less compact targets, i.e. targets which are more or less porous, particles tend to spark off during the sputtering process. These particles then evaporate and lead to arcing (see above). Finally, a fine-crystalline structure is necessary for the target, in order to achieve a sufficiently uniform deposition of the layer and a uniform erosion of the target. In the case of sputtering materials where the sputtering rate depends on the orientation of the crystals, a coarse-crystalline structure can lead to a non-uniform layer. The necessary level of purity of the material, its uniformly high density, a fine-

crystalline texture and the even distribution of the alloy components (if applicable) must be ensured by expert metallurgical preparation of the raw materials as well as in the target production process.

For conventional DC or AC sputtering, the target material (in the form of sheet metal with a thickness of 3 to 5 mm) is soldered directly onto the cathode tube. In the early days of sputtering, at the beginning of the 1960's, the target material used to be flame-sprayed onto the cathode tube. Today's targets for planar magnetron cathodes are 10 to 20 mm thick. They are attached to holding plates which are screwed onto the cathode body. Holding tubes are used in the same way for rotatable cathodes. When attaching the holding plate or tube to the cathode body, care must be taken to ensure a good heat transfer from the target to the cooling medium-filled cathode body. This is because, as mentioned in the previous chapter, approximately 75 % of the energy used for the process is transformed into heat, which has to be removed to prevent overheating or melting of the targets. In addition, a good electrical contact is necessary, as currents of up to 100 A flow between the target and the cathode body.

Several joining techniques are employed to attach the target material to the holding plates or tubes for magnetron cathodes. The most common ones are described below.

Cast-on technique

This technique is used with metals which have a low melting point, e.g. tin and indium targets. The molten metal is poured into a mould which is placed onto the holding plate, usually in a vacuum (to avoid bubbles and blowholes) or in a protective atmosphere. The cooling process must be controlled, in order to achieve the fine-crystalline structure. After cooling, the target is given its final shape by means of milling and grinding. Figure 4.2.1.6.1 shows the cross-section of a target cast on a holding plate which is screwed onto a planar magnetron cathode.

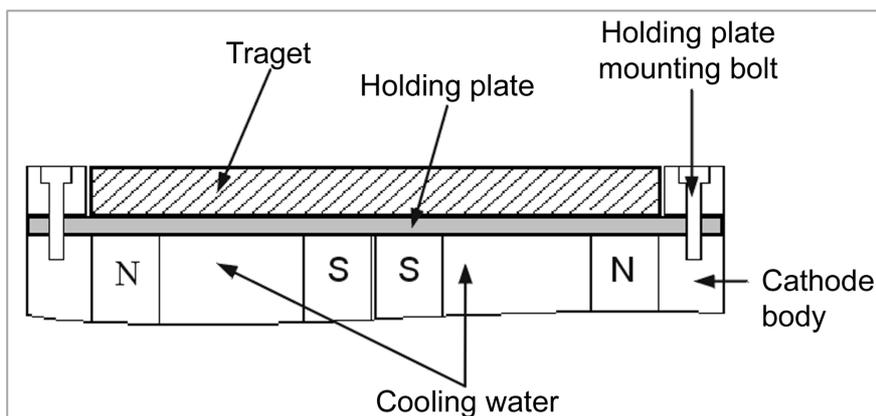


Figure 4.2.1.6.1: Cross-section of a cast-on target screwed onto a planar magnetron cathode

Solder-on technique

The solder-on technique, also called bonding, is used either with metals which have a high melting point (e.g. silver, gold, copper, zinc, titanium and aluminium), which can be produced in sheet form, or with materials which can only be produced in the form of bars

because of their brittleness or other metallurgical properties. The sheets made from metals with a high melting point are manufactured by means of metal working techniques (rolling, extruding, milling, cutting etc.) and soldered onto the holding plate. The bars are manufactured by casting into a mould (e.g. for silicon targets) or by hot isostatic pressing of powder (e.g. for certain bismuth-manganese alloys) and finally soldered onto the holding plate. Hot isostatic pressing is appropriate for metals which are known to be difficult or impossible to cast, such as materials with high melting points, alloys made from components with different vapour pressures or materials with a tendency to separate during cooling. Figure 4.2.1.6.2 shows the cross-section of a target soldered onto a holding plate which is screwed onto a planar magnetron cathode.

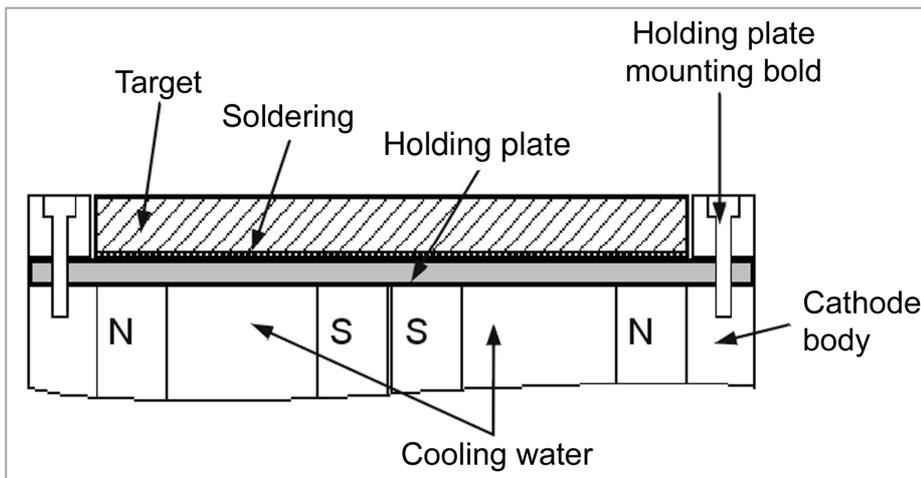


Figure 4.2.1.6.2: Cross-section of a soldered-on target screwed onto a planar magnetron cathode

In order to avoid the formation of alloys with a low melting point, the target surface to be soldered is coated prior to soldering with a strongly adhesive, solderable blocking layer, by means of sputtering or electroplating. Furthermore, this blocking layer is intended to prevent the target from being contaminated with the soldering material, i.e. it blocks diffusion. Because there is a danger of blistering with large-area solder surfaces, the target is soldered onto the holding plate in a vacuum. Air-filled bubbles and blisters impair the thermal contact between the target and the cathode body so that the target overheats during sputtering and is destroyed. The bubbles and blisters can be identified by ultrasonic detection methods. In order to avoid mechanical stresses due to different coefficients of thermal expansion for the target material and the holding plate, the cooling process must be carefully controlled.

Screw-on technique

For some sputtering processes the target sheet or the target bar can be screwed directly onto the cathode body. However, in order to improve thermal contact, in some cases a heat-conducting graphite foil should be placed between the target and the cathode body.

Flame-spray and plasma-spray technique

With this technique, the target material is melted by a flame or by arcing and is then sprayed onto the holding plate or holding tube, where it fuses. This technique was used to make gold and bismuth targets for conventional sputtering until the 1990s. The metals were sprayed onto the cathode tubes with an acetylene/ oxygen flame-spray gun. Gold was fed into the gun in the form of wire, bismuth in the form of powder. Today, the plasma-spray technique, which is very similar to the flame-spray technique, is usually applied to produce sputtering targets, because higher melting temperatures and purer targets can be achieved. The spray gun is used with an arc discharge in a controlled, inert (if necessary oxidic), low-pressure atmosphere. The target material is passed into the arc discharge in the form of powder at an angle of approximately 15°. The powder particles are melted on their surface and propelled onto the holding plate or tube where they melt together. In order to achieve the required density of the target material the grain size of the powder and the spraying conditions must be adjusted so that they are optimal. It may be necessary to subject the sprayed targets to a subsequent sintering process.

The plasma-spray technique is a very flexible manufacturing method for targets. Almost any material can be processed for almost any target form. This method is particularly appropriate for the production of targets with a circular cross-section, as used for rotatable magnetron cathodes (see Figure 4.2.1.5.2.5). A particular advantage of the flame/ plasma-spray technique is that it allows the target profile to be shaped according to the erosion profile, i.e. the target material can easily be applied more thickly in areas where erosion is greater during the sputtering process, due to the ion lens effect. In this way, a much higher target yield can be attained and the target lifespan is extended considerably. Furthermore, worn targets can be re-used by means of this technique because 'sputtering grooves' can be filled in, which is often less expensive than producing entirely new targets. Targets with a thickness of 5 to 12 mm are produced today by means of plasma-spraying.

As has been mentioned previously, the majority of the electric power used in the sputtering process is transformed into heat and has to be removed from the targets. Thus, a good thermal contact between target and cathode body is of major importance. As well the thermal conductivity of the target material itself is no less important, because the heat generated at the target surface has to be conducted through the target to the cathode body, where it is removed by the cooling medium. For this reason, the target thickness and sputtering power density have to be carefully matched, particularly when using materials with low thermal conductivity, such as bismuth.

Since sputtering for flat glass coating purposes is carried out exclusively using DC voltage and low/ medium-frequency AC voltage, it is not only the electrical contact to the cathode body, but also the electrical conductivity of the target material itself which must be sufficiently high. The electrical conductivity of the metals commonly used for flat glass coating is sufficiently high. However, materials with low conductivity, e.g. silicon, can be doped, for instance with boron or about 10 % aluminium, in order to increase their electrical conductivity. In the latter case the dopant causes the additional side effect of reducing the brittleness of the silicon target.

4.2.1.7 Coating plants and processes using sputtering technology for large-area flat glass coating

Figure 4.2.1.3.1 shows the components of a sputtering plant. It basically consists of a vacuum chamber in which the cathode and substrate are situated, a sputtering gas inlet valve, a set of vacuum pumps which generate the low pressure necessary for the gas discharge process and a power supply unit with which the gas discharge is ignited. Using a simple design of a plant as shown in Figure 4.2.1.3.1, the sputtering process can be studied under laboratory conditions and also small-scale coatings can be carried out.

For industrial-scale large-area flat glass coating processes, however, coating plants are necessary which have to be carefully adapted to the properties of the substrate to be coated (in this case flat glass panes of a size up to 3.21 m x 6.00 m) and the desired coatings, as explained in Chapter 2.4 and 4.1. This affects not only the coating tools, i.e. the rod cathodes and their environment in this case, but also the design and arrangement of the vacuum chamber(s) and the positioning of the rod cathodes inside them, as well as the conveyance of such large-area panes into and out of the coating plant. A suitable cleaning plant for large-area panes (as described in Chapter 3.4.2), which is added to the sputtering plant, belongs to the whole plant concept as well. Furthermore, suitable gauging devices for the vacuum and the gas admission, together with measuring equipment for quality control after the panes have been coated, are also all essential components of the coating plant. After installing the plant components, it is necessary to find and set the optimal process parameters to run the coating process, i.e. the pressure and composition of the sputtering gas, the sputtering voltage, the relative velocity of panes or cathodes etc. Only when the coating plant is complete, with all its components and all the optimised process parameters, the production process can take place, i.e. the sputter deposition process is ready for production.

There are two types of plants which are used for flat glass coating: one-chamber plants, also called 'batch plants', and multi-chamber plants, also called 'in-line plants'. In a batch plant, a number of panes (a batch), is coated at the same time, whereas in an in-line plant the panes pass continuously through several vacuum chambers, one after another (in line). Another difference between the two plant types lies in the kinematics during the coating stage. In a batch plant the panes are fixed and a rod cathode array moves along them. In in-line plants, however, the panes are conveyed below fixed rod cathodes.

4.2.1.7.1 Sputter deposition with batch plants

Figure 4.2.1.7.1.1 shows the first flat glass sputtering plant, a batch plant employing the principle of conventional 50 Hz AC sputtering, which was built by L. HOLLAND of Edwards (GB) for the Belgian firm Glaverbel in the early 1960's. It is based on conventional sputtering with AC high voltage at 50 Hz frequency. During the sputtering process, the panes to be coated were fixed in a supporting frame which rotated, in a horizontal position, above the cathodes which were arranged in sectors. This plant turned out to be a disaster because the panes bowed into the dark space which partially extinguished the gas discharge. The panes were consequently coated, for example, only towards the edges of the supporting frame, i.e. the layer thickness varied greatly across the pane surface. The design of the plant was upscaled from a laboratory coater to a commercial-scale coater.

This serves as an early example of the fact that a fully functional laboratory-scale system cannot be transferred to a commercial-scale plant without consideration of the different substrate size and properties. Eventually, Glaverbel modified the plant so that the panes were fixed in vertical supporting frames with rod cathodes conveyed along them in AC mode.

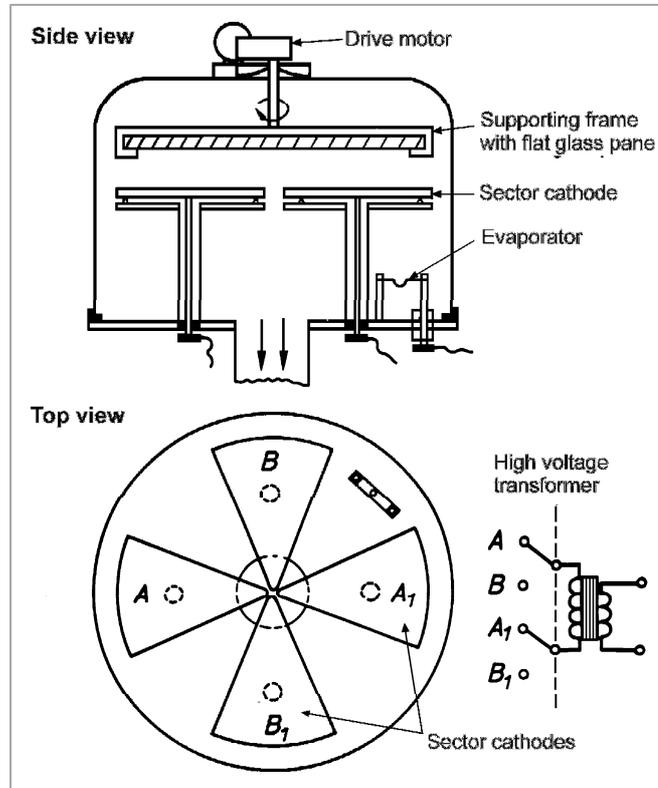


Figure 4.2.1.7.1.1:
Diagram of the first flat
glass sputtering plant
(source: HOLLAND)

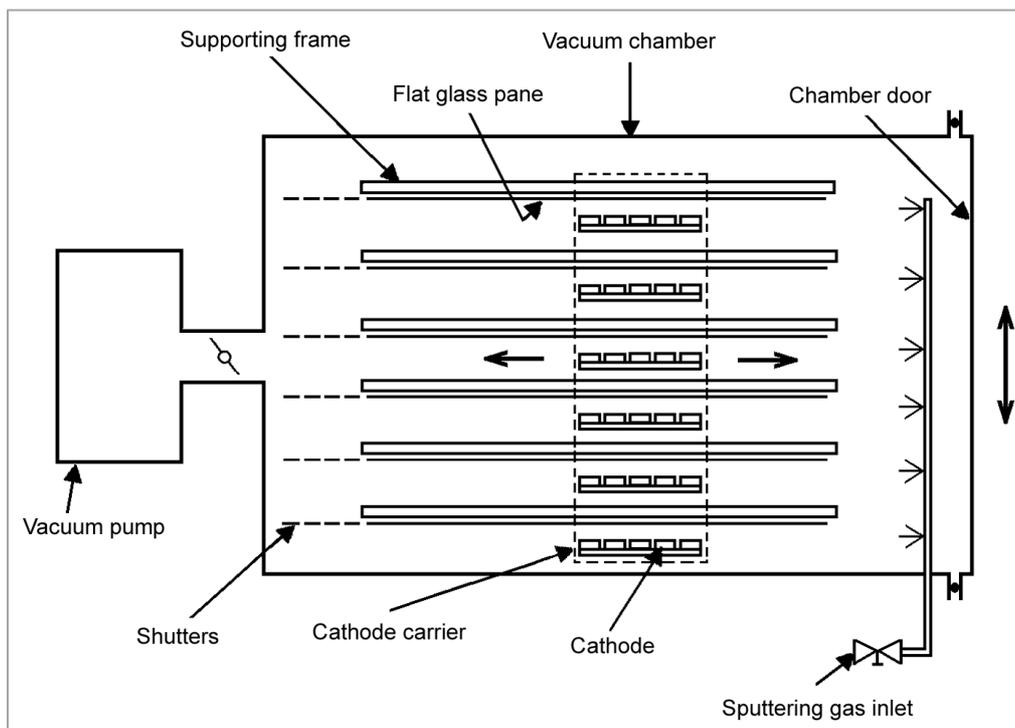


Figure 4.2.1.7.1.2: Diagram of a batch-type flat glass sputtering plant
(source: INTERPANE LAUENFÖRDE, Germany)

Figure 4.2.1.7.1.2 shows the diagram of the final stage of these batch-type technology plants, with which panes of a size of up to 3.21 m x 6.00 m were coated with silver-based low emissivity coatings to produce heat-insulating glass for the first time in 1982. The panes to be coated are fixed onto up to six supporting frames and positioned in the coating chamber parallel to one another, at an angle of about 6° from the vertical line. During the sputtering process rod cathodes, mounted on a cathode carriage, are moved along the panes. It is important that the sputtering gas is admitted opposite the vacuum pump suction opening, so that interfering gas impurities, known as residual gases, are constantly swept away. The low pressure necessary with a residual gas-free vacuum for sputtering can thus be generated without high-vacuum pumps, i.e. by means of simple mechanical pumps, such as Roots pumps. Cathodes with the same target material are placed in a row in the cathode carriage, at right angles to the direction of pane conveyance. When coating a layer system, this arrangement allows several individual layers to be applied by switching the power supplies over to the appropriate cathode rows. The AC mode (see Figure 4.2.1.5.1.2), using a simple high voltage transformer directly connected to the mains, has been widely replaced by the use of the DC mode (see Figure 4.2.1.5.1.1). This development has taken place since the late 1970s, as demands for highly uniform coatings increased. Controllable low-frequency power supplies with adequate output power were not available at that time.

The process of coating flat glass in a batch plant, for example with a low emissivity layer system on a basis of silver for heat-insulating glass (see also Chapter 5.1.3.1, Part II), is shown in the form of a pressure-time curve in Figure 4.2.1.7.1.3.

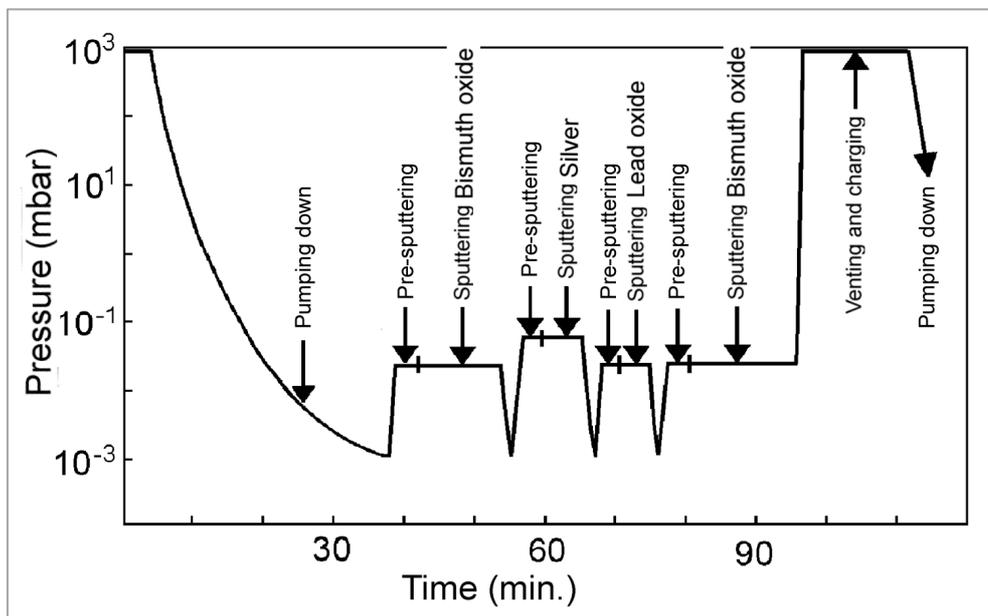


Figure 4.2.1.7.1.3: Pressure / time curve for coating low emissivity layer systems on the basis of silver in a batch-type flat glass sputtering plant

After positioning the panes mounted on the supporting frames in the vacuum chamber, the chamber door is tightly closed and the vacuum pumps are used to attain a pressure of about 10^{-3} mbar. Then the reactive sputtering gas for the first coating stage (bismuth oxide layer in this example) is admitted so that the pressure rises again to a sputtering pressure

of about $2 \cdot 10^{-2}$ mbar. The cathode row used for the first layer is then conditioned by igniting the gas discharge while the cathodes are positioned in front of the pre-sputtering shutter. Next, the first layer is deposited by an appropriate number of cathode passages. In order to apply the second layer, the chamber is again briefly evacuated and brought to the above-mentioned low pressure. Then another sputtering gas (in this example an inert gas for non-reactive sputtering of silver) is admitted until the working pressure of $6 \cdot 10^{-2}$ mbar is reached. The power supplies are switched to the second row of cathodes, the cathodes are also conditioned in front of the pre-sputtering shutters, and finally the second layer is deposited in the same manner as the first one. For further layers, e.g. a lead oxide blocking layer and a final bismuth oxide layer to complete the layer system, these steps are repeated accordingly. After the deposition of the entire layer system, the vacuum chamber is vented and charged, i.e. the coated panes are unloaded from the chamber which is then reloaded with uncoated panes.

Batch-type sputtering plants for the deposition of a four-layer, low emissivity coating on the basis of silver onto flat glass panes up to 3.21 m x 6.00 m have coating capacities of up to 500,000 m² per annum. Both cathode types for conventional sputtering (see Figure 4.2.1.5.1.1) and magnetron sputtering (see Figure 4.2.1.5.2.1) can be used in batch-type systems. With the latter, however, high-vacuum pumps, e.g. turbo-molecular pumps, have to be used, in order to attain sputtering pressures of approximately 10^{-3} mbar. It should be noted that, because of excessive pane heating due to electron bombardment, during conventional sputtering only large-area flat glass which meets strict requirements regarding permanent residual stress is suitable (see Chapter 4.2.1.5.1). Figure 4.2.1.7.1.4 shows a batch-type sputtering plant in operation.



Figure 4.2.1.7.1.4: Batch-type sputtering plant for jumbo size flat glass panes
(source: INTERPANE LAUENFÖRDE, German)

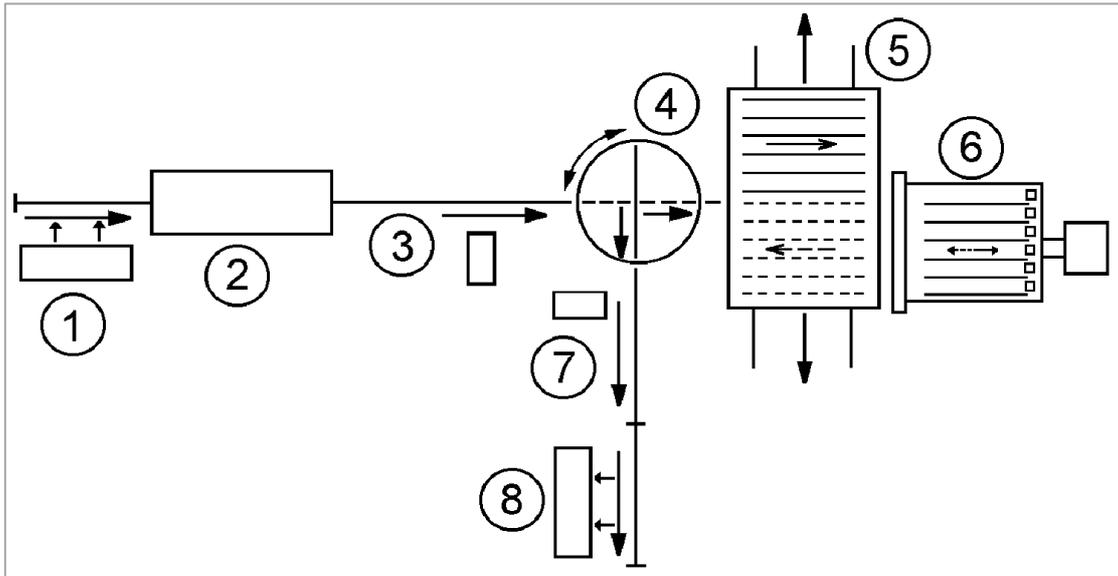


Figure 4.2.1.7.1.5: Production flowchart for flat glass sputter coating with a batch plant

- 1: Feeding the panes to be coated 2: Washing machine 3: Visual check of the cleaned panes
 4: Mounting/ dismounting the panes to/ from the supporting frames 5: Supporting frame carriage
 6: Coating chamber 7: Final inspection of the coated panes 8: Stacking the finished panes

Figure 4.2.1.7.1.5 shows the production flowchart for flat glass sputter coating with such a plant. The panes, with dimensions of up to 3.21 m x 6.00 m, are positioned on a conveyor belt, pass through the washing machine and, after a visual cleanliness check, enter the mounting equipment which can be revolved around a vertical axis and the height can be adjusted. By means of this equipment the panes are mounted onto the supporting frames. The mounted panes are stored in a frame carriage from where they are pushed into the coating chamber. After the panes have been coated, they are drawn with the supporting frames out of the chamber onto the frame carriage, from which they are positioned again in the mounting equipment where they are removed from the supporting frames. Then the coated panes undergo a final inspection on the exit conveyor belt before they are stacked.

Until the early 1990s batch plants were used predominantly. From the early 1980s, a growing market for heat-insulating glass implicates that there was an increasing demand for much higher production capacity. The quality requirements for low emissivity coatings have also increased. As a result there has been a growing tendency to replace batch plants with in-line plants which can fulfil the advanced requirements. The general concept for these in-line plants dates from the 1970s.

4.2.1.7.2 Sputter deposition with in-line plants

Figure 4.2.1.7.2.1 shows a diagram of a modern in-line flat glass sputtering plant using magnetron cathodes. Flat glass panes of up to 3.21 m x 6.00 m pass continuously through a number of in-line positioned vacuum chambers on a horizontal roller conveyor belt. The first chamber of the plant serves as the lock-in chamber, which can be tightly closed using slot valves at its entrance and exit. For coating flat glass panes of the above-mentioned dimensions (or a corresponding number of cut-to-size panes), the pane is conveyed into the

lock-in chamber through the opened entrance slot valve. Thereafter the slot valve is closed and the chamber is pumped down to approximately 10^{-1} mbar. As soon as this low pressure is achieved, the exit slot valve opens and the pane is conveyed to the transfer chamber (also called buffer chamber) in which the pressure is reduced further to approximately 10^{-2} mbar. At the same time, the lock-in procedure for another pane is performed, while the previous pane passes continuously in line from the transfer chamber to the pumping and coating chambers, the number and design of which depends on the required layer system and on the desired plant capacity. After the deposition of the layer system the pane enters the exit transfer chamber in which the pressure is raised again and finally passes into a lock-out chamber in which atmospheric pressure is reached again in a manner analogous to that of the lock-in procedure.

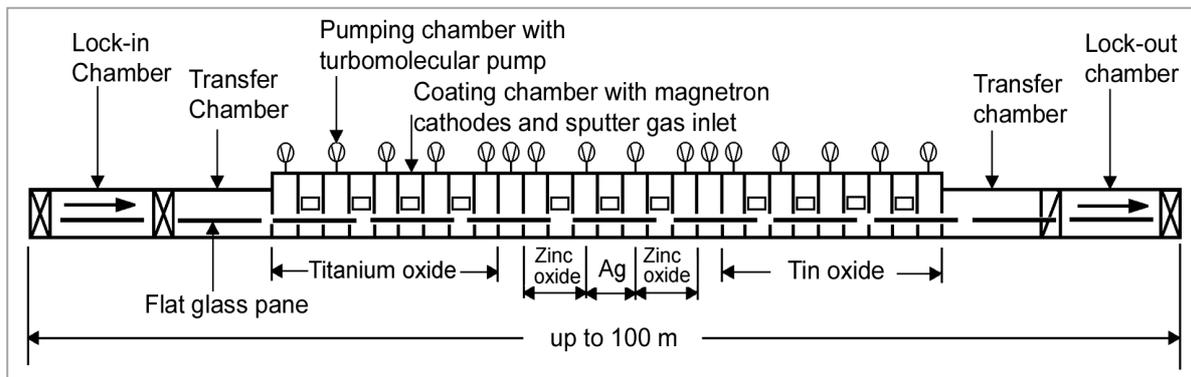


Figure 4.2.1.7.2.1: Diagram of a modern in-line flat glass sputtering plant with magnetron cathodes

Each sputtering chamber contains the cathode or dual-cathode arrangement (see Figure 4.2.1.5.2.3 or 4.2.1.5.2.8) with the gas inlet system. Each side of a coating chamber is connected to a process pumping chamber equipped with turbo-molecular pumps. Next to the process pumping chambers there are installed an isolation chambers, also equipped with turbo-molecular pumps. The isolation chambers are connected to the process pumping chambers by a slot which acts as a flow resistor. These slots allow the panes to enter and exit the coating chambers, but also enable the sputtering pressure and the sputtering gas composition to be maintained at certain levels. In this way it is possible to set and control the gas discharge of each cathode individually. If the sputtering pressure and sputtering gas composition vary greatly from one coating chamber to the next, as is the case when a coating chamber operating in the reactive mode is followed by a chamber which operates in the non-reactive mode or vice versa, several isolation pumping chambers may be installed in line so that the gas atmospheres of the two coating chambers are fully separated. For plants with very short lock-in/ lock-out cycles (e.g. ≤ 45 s), i.e. high capacity plants, two lock-in and lock-out chambers in succession are necessary, in order to reduce the pumping time. A specific problem associated with the length of the rod cathodes that are now usual in flat glass coating is the distribution of the sputtering gas within the sputtering chamber. It is determined both by the design of the cathode and its surroundings and also by outgassing of sputtering chamber itself, and may need to be adjusted individually for each particular coating arrangement.

A further problem of in-line plants is that the entire plant must be vented for maintenance to be carried out inside or for worn targets to be replaced. Whereas batch plants can be

worked on while loading a new batch (resulting in shorter downtimes), the coating process of in-line plants must be interrupted for several hours. After completion of the maintenance work, they have to be pumped down and restored again to the required coating conditions. The adsorption of humidity by the inner chamber walls while the chambers are open forms the most serious problem. All these points are disadvantages of in-line plants. However, downtimes for conditioning a coating plant after maintenance at atmospheric pressure can be reduced by means of low temperature condensers, also known as cryopumps, and/ or the use of coating materials which can be sputtered at limited water vapour concentrations without the layer properties being noticeably altered, if the sputtering parameters are adjusted adequately. Bismuth oxide (BiO_x) is an example of such a material.

The enlargement of the target surface area with progressive target erosion creates a general problem for both conventional and magnetron sputtering processes (see also Chapters 4.2.1.5.1 and 4.2.1.5.2). Owing to this phenomenon it becomes necessary for the sputtering parameters to be adjusted constantly. Whereas in the non-reactive mode only the sputtering voltage or sputtering power have to be altered in order to keep the sputtering rate at a constant level, maintaining a constant sputtering rate in the reactive mode is more difficult. A changing sputtering rate may affect not only the layer thickness, but also the stoichiometry and hence the physical properties of the layer. In order to keep the sputtering rate constant, at least two of the three process parameters (sputtering voltage or sputtering power, sputtering gas composition and relative movement of cathode or pane) must be regulated. Figure 4.2.1.7.2.2 shows the regulation of cathode carrier velocity and oxygen proportion in the sputtering gas atmosphere for the reactive sputtering of bismuth oxide with a batch-type coating plant depending on the batch number.

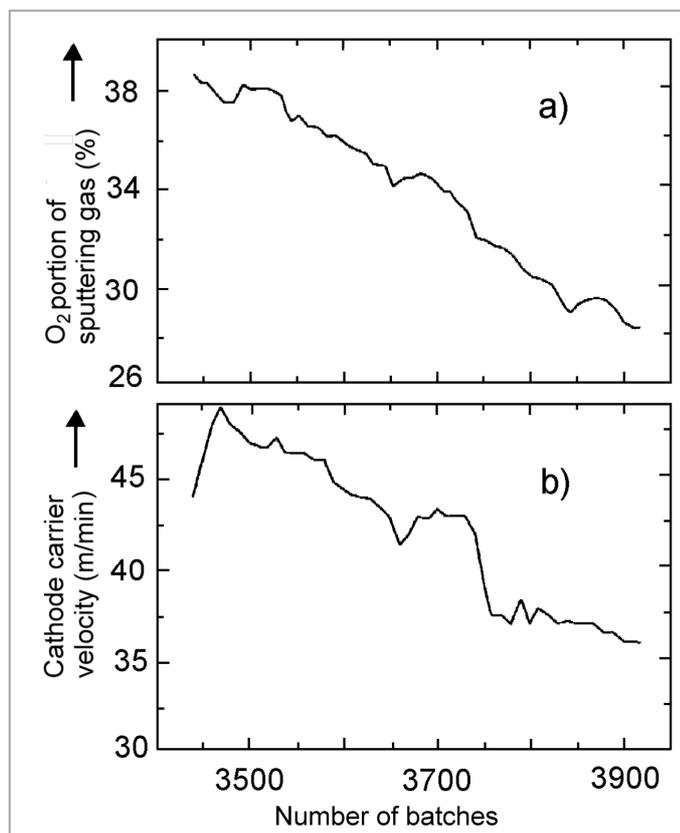


Figure 4.2.1.7.2.2:

Oxygen levels in the sputtering gas atmosphere (a) and cathode carrier velocity (b) depending on the number of batches for reactive sputtering of bismuth oxide with a batch-type coating plant

(source: STOLLENWERK)

In modern in-line coating plants the sputtering voltage or sputtering power and the partial pressure of the oxygen are usually regulated. Since the target surface enlargement is much more distinct for magnetron sputtering than for conventional sputtering (compare 4.2.1.5.1.1 and 4.2.1.5.2.1), sputtering parameters with magnetron cathodes have to be adjusted at shorter intervals.



Figure 4.2.1.7.2.3 Photo of a modern in-line magnetron sputtering plant
(source: INTERPANE E&B, LAUENFÖRDE, Germany)

Figure 4.2.1.7.2.3 shows the photo of a modern in-line magnetron sputtering plant for flat glass. Today, plants like this are equipped with up to 25 magnetron cathodes and are up to 60 m long. Panes of up to 3.21 m x 6.00 m, can be coated in these plants. They have a coating capacity of up to 8 million m² per year, which equals roughly the capacity of a modern float glass production line (see Chapter 1). They are used world-wide, predominantly for the production of low emissivity layer systems on the basis of silver (see Chapter 5.1.3.1, Part II) applied in heat-insulating glass and for the production of solar-control layer systems applied in solar-control glass (see Chapter 5.2, Part II). As explained in Chapter 4.2.1.5.2, the panes are not heated up by electron bombardment when coated using the magnetron technique and therefore no warping of the float glass takes place during the coating process. This is a great advantage of the magnetron technology, particularly for jumbo size panes.

In magnetron plants of a similar design are also used to deposit transparent conductive oxide (TCO) layers, such as ITO (see Chapter 5.1.2.1, Part II), and anti-reflection layers (see Chapter 5.3.1, Part II). In order to achieve a low sheet resistance, TCO coating processes require the panes to be heated up to about 300°C. Because it is very difficult to heat jumbo size panes evenly in vacuum conditions to such high temperatures and subsequently to cool them, serious warping in the panes is to be expected. Therefore, high-quality TCO layers can only be applied to smaller panes, currently with a maximum area of 2.6 m² (see also Chapter 1.4.3).

Figure 4.2.1.7.2.4 shows production flowchart for flat glass coating with an in-line magnetron plant.

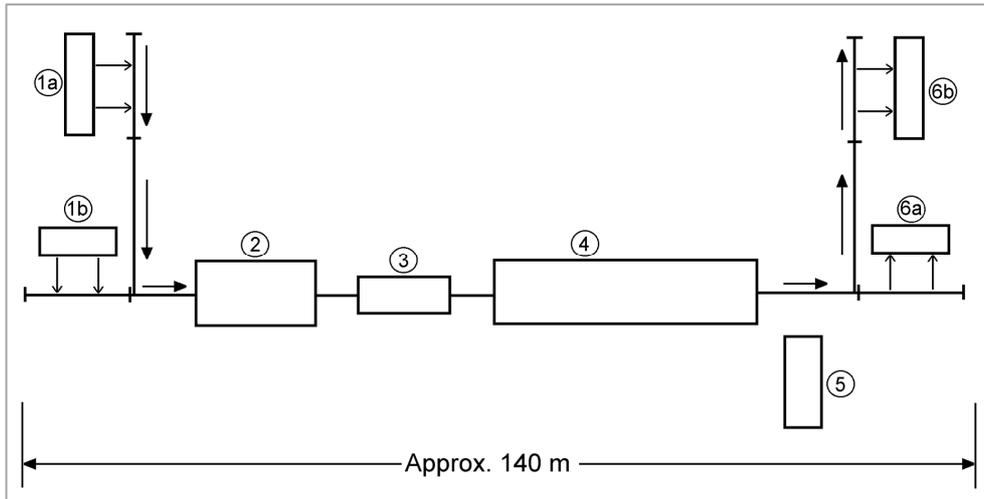


Figure 4.2.1.7.2.4: Production flowchart for coating of flat glass with an in-line magnetron plant

- 1a: Loading the jumbo size panes to be coated 1b: Loading cut-to-size panes to be coated 2: Washing machine 3: Visual check of the cleaned panes 4: Coating plant 5: Final inspection of the coated panes 6a: Stacking the finished cut-to-size panes 6b: Stacking the finished panes

After being positioned on the horizontal conveyor belt, the panes pass through the washing machine and are inspected visually for cleanness. Then they enter the coating plant. Once the layer system has been deposited, the panes undergo a final inspection and are then stacked ready for transportation and further processing.

The quality control of individual layers and the entire layer system during and after the coating process depends on the type of layer. Today, for layer systems on the basis of silver comprising up to four single layers, as used for heat-insulating and solar-control glass (see Chapter 5.1.3.1, Part II), the spectral transmittance $\tau(\lambda)$ is controlled by permanently mounted photometers in-line after deposition of the first layer, the so-called adhesion layer, and after deposition of the third layer, the silver layer. The final inspection of the complete coating occurs immediately after the coated panes have been locked out of the vacuum system. Important properties of the layer system, such as the spectral transmittance $\tau(\lambda)$ in the visible range, the colour coordinates L^* , a^* , b^* in reflection and the infrared reflectance, are established by means of photometers. Instead of measuring the infrared reflectance, the corresponding sheet resistance (R_{\square}) of the layer can be determined at several points across the entire pane area with a conductivity measuring device (see Chapter 5.1.1, Part II). The colour uniformity of the whole coated pane is normally also evaluated visually at this stage, by inspecting the reflection pattern of a diffusely illuminated white surface, the so-called 'artificial sky'. The layer adherence can be tested by wiping the pane manually with a clean cloth. All these checks are performed on every pane. The coating process is monitored from a control room. In addition, samples of coated glass are taken from the running process at regular intervals, according to a testing plan, and examined in a quality control laboratory where all characteristic optical and thermal parameters of the coated glass are also tested once again. The quality control laboratory also carries out tests to analyse resistance to ageing and processability (see also Chapter 5.6, Part II), i.e. subsequent processing.

4.2.2 Thermal evaporation

4.2.2.1 Applications of thermal evaporation for coating flat glass

Thermal evaporation was very important from the 1960's to the 1980's, i.e. during the initial years of coating flat glass with vacuum-based processes, because considerable experience had been gained with this technology in other sectors, which could be transferred to flat-glass coating. However, due to its limited production capacity and for economic reasons, thermal evaporation was gradually replaced by sputtering as the main coating process for flat glass. It is now used by only a few companies throughout the whole world. The main application for thermal evaporation was and is for solar-control coatings applied in solar-control glazing (see Chapter 5.2, Part II). Today, it is still used to replace defective solar-control glazing in buildings where this technology was used in the past for the coatings, and for some special applications of coated flat glass.

In its heyday, this process was used to deposit about 750,000 m²/a of solar-control coatings around the world. In addition, it was used until the beginning of the 1990's to produce aluminium and low-reflectance chromium mirrors. The aluminium mirrors were used as front-surface mirrors in high-quality optical instruments and as back-surface mirrors as a substitute for silver mirrors in countries of the former Eastern bloc. The chromium mirrors are used as low-reflectance rear-vision mirrors in cars. However, aluminium and chromium mirrors for these purposes are also mainly manufactured by sputtering today. Single-chamber systems are used in batch operation to coat flat glass by thermal evaporation. In two cases, multiple-chamber systems were also used. However, only a few single-chamber systems are in operation today.

Typical materials for coating flat glass by thermal evaporation are:

- the metals gold, silver, copper and aluminium
- metal alloys such as nickel chrome (NiCr) or those containing chromium, aluminium and iron, and
- the dielectric layers, zinc sulphide (ZnS) and silicon oxide (SiO_x).

As thermal evaporation requires vacuum conditions, it must be done off-line, i.e. independently of the flat glass manufacturing (see footnote 1). It should be noted that this type of coating technology is very flexible with regard to the possible multi-layer configuration and the properties which can be achieved with glass coated in such a manner. Thermal evaporation using batch systems is particularly suitable for coating niche products with small batch quantities.

4.2.2.2 Fundamentals of coating by thermal evaporation

The English physicist, Faraday, was the first to report the deposition of the thin films by thermal evaporation. Around 1857, about the same time as sputtering was discovered, he prepared thin metal films from exploding metal wires in an inert gas atmosphere at reduced pressure.

For thermal evaporation, energy is added to the coating material in the form of heat. When heating up its vapour pressure increases, i.e. it evaporates noticeably. The evaporation process can occur above molten material, i.e. from the liquid form of the material, just as when water boils, or also by sublimation, i.e. the direct transition from the solid phase to the gas phase, as can be observed when washing dries in winter at temperatures below 0 °C. Coating occurs when the vapour is allowed to condense on a substrate, a pane of flat glass in our case.

During the coating process, the evaporation occurs under vacuum. The evaporation rate W of a material is of interest for commercial coating. It describes the amount of material (in g) which evaporates from unit area (cm^2) as a function of time (s). If the evaporation rate is known, the required amount of coating material and the area of the evaporation source for a given film thickness can be estimated. The Langmuir equation describes the evaporation rate as follows:

$$W = 0.044 * p_s * (M / T)^{1/2}$$

where p_s is the saturation vapour pressure, M is the molecular weight of the coating material and T is the absolute temperature of the evaporating material. The saturation vapour pressure p_s of a material depends on its temperature and can be derived from the Clausius-Clapeyron equation. The following approximation can be obtained, which applies for vapour pressure up to about 1 mbar:

$$p_s \sim e^{-B/T}$$

where B is a quantity depending on the heat of evaporation for the coating material in question. Due to the exponential dependence of the vapour pressure on temperature, relatively small temperature fluctuations can result in wide variation of the vapour pressure and thus also the evaporation rate. For coating purposes, this means that sophisticated controls must be implemented in order to maintain a constant evaporation rate during the coating process, which is essential to obtaining reproducible coating properties for a set of coatings.

In Figure 4.2.2.2.1 the evaporation rate versus the temperature is shown for several materials used to coat flat glass. In practice, the degree of freedom for evaporation rates is limited. On the one hand, if evaporation is too slow, undesirable reactions of the coating material with residual gas (e.g. O_2 , N_2 , H_2O or also oil vapour) in the evaporation chamber occur. These undesirable reactions can be suppressed to a limited extent by diluting the residual gas atmosphere with inert gases like argon. On the other hand, if evaporation is too rapid, unevenly thick coatings and explosive evaporation of the coating material may result, i.e. the material does not evaporate but is sprayed. For thermal evaporation, the evaporation rates are usually in the range from 10^{-4} to 10^{-3} g/(cm^2s). If, for example, a molecular weight of 100 and a temperature of the evaporation source of 1800 K are assumed, corresponding to a usual evaporation temperature, the resulting vapour pressures range from 10^{-2} to 10^{-1} mbar.

As for sputtering, the energy of the incident particles is decisive for film growth on the substrate. Thermal evaporation differs appreciably from sputtering in this aspect. The energy of the thermally evaporated particles E_D is described well with the following approximated equation:

$$E_D = 1.5 * k * T$$

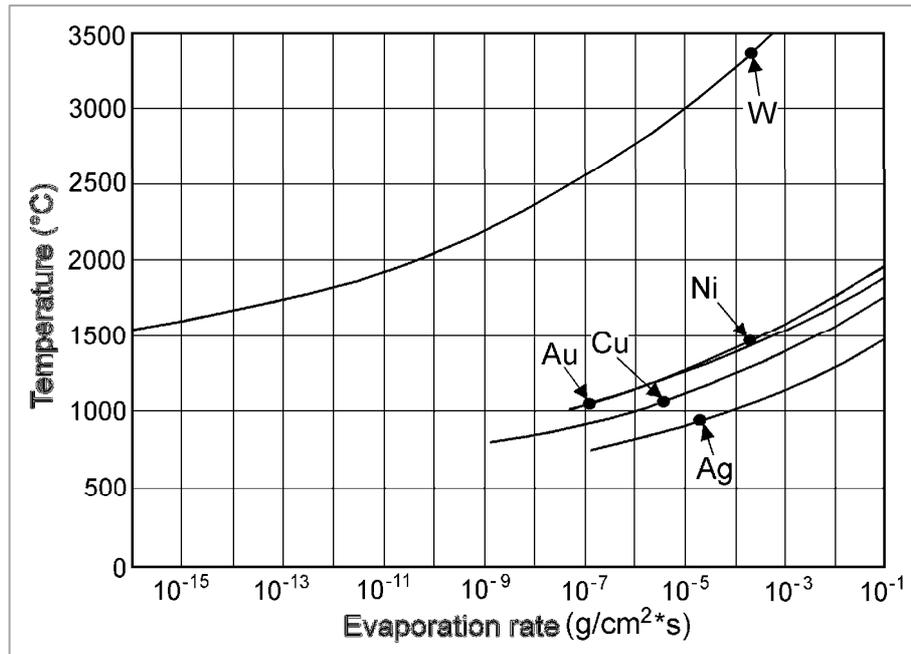


Figure 4.2.2.2.1 Evaporation rate versus temperature for several materials used to coat flat glass

where k is the Boltzmann constant ($8.62 \cdot 10^{-5}$ eV/K) and T is the absolute temperature of the evaporating material. If a temperature of 1500 K is assumed for the evaporating material, the average energy of the evaporating particles is found to be about 0.2 eV. Thus, the energy of the evaporating particles is about a factor 20 lower than for sputtering (see Chapter 4.2.1.3).

In order for the evaporated particles, with their low energy and thus also low velocities, to reach the substrate, it is important that they are not slowed down by collisions with residual gas particles in the evaporation chamber. For this reason, either the distance between the evaporation source and the substrate must be short or the pressure in the vacuum chamber must be correspondingly low. As the evaporation source is maintained at a very high temperature, it should not be located too close to the substrate, so that the second option must be taken. Very low pressures are applied for evaporation, which are usually between 10^{-6} and 10^{-5} mbar for a distance of 30 to 70 cm between the evaporation source and the substrate. In comparison to sputtering, the pressure for thermal evaporation is a factor of 100 lower and the distance between the source and the substrate is a factor 2 to 10 higher (see Chapters 4.2.1.5.1 and 4.2.1.5.2).

Due to the low energy of the particles incident on the substrate, thermally evaporated coatings generally do not adhere as well as sputtered coatings do (see also discussion in Chapter 2.3). In order to improve adhesion, it is thus usual to expose the substrate surface to a gas discharge before coating by thermal evaporation. This procedure is intended not only to clean the surface of water and oil residues by ion bombardment, but also to create nuclei for film growth, improving the adhesion coefficient α_s of the substrate (see Chapter 4.2.1.3). Furthermore, because of the low energy of the incident particles the coatings results in less crystallinity than by coating with sputtering under otherwise comparable conditions (e.g. identical substrate temperature and processing pressure; see structure zone models of Movchan and Demchisin and Thornton in Chapter 4.2.1.3). This property can be improved to a limited extent by an appropriate choice of processing parameters. In

order to produce coatings of the required even thickness on large-area substrates such as flat glass, the coating material process must be evaporated as slow as possible, so that the particles incident on the coating surface can distribute themselves as evenly as possible by significant surface diffusion.

A further difference to sputtering is that alloy components can evaporate at different rates corresponding to their partial pressures at the high evaporation temperatures used, such that the coating has a different chemical composition to the original material. The high temperatures can also lead to dissociation of the molecules of chemical compounds, and thus to deviations in the stoichiometry of the deposited coating. Thus, thermal evaporation is less suitable than sputtering for coating with alloys or chemical compounds. Nevertheless, as mentioned in Chapter 4.2.2.1, thermal evaporation is used to coat flat glass with alloys such as nickel chrome or chemical compounds such as zinc sulphide or silicon oxide (SiO_x). However, it is necessary to test whether and how an alloy or chemical compound can be thermally evaporated, quantitatively and stoichiometrically, for each individual case. For example, chemical compounds which have dissociated may recombine if the evaporation process is slow enough.

Thermal evaporation can also be carried out in a reactive atmosphere, i.e. containing oxygen, nitrogen or sulphur. However, this type of coating process has not been applied up to now to coat large-area flat glass.

4.2.2.3 Technology for coating flat glass by thermal evaporation

Figure 4.2.2.3.1 shows the diagram of a coating system based on thermal evaporation.

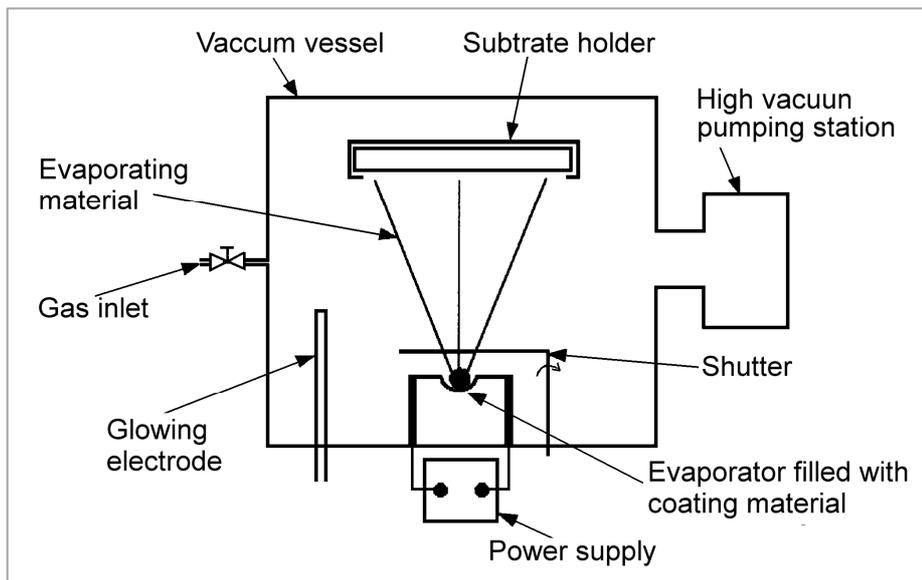


Figure 4.2.2.3.1 Diagram of a coating system based on thermal evaporation.

An evaporation source is installed in a vacuum chamber that is maintained at a pressure of 10^{-5} to 10^{-6} mbar by high-vacuum pumps, which also appropriately corresponds to the coating plant for large-area coating. The substrate, in our case the pane of flat glass, is positioned with a substrate holder 30 to 60 cm above the evaporation source. The evaporation source is covered with a shutter during the initial heating process. The vacuum

chamber also contains an electrode for surface cleaning by ion bombardment. Thermal evaporation in an inert or reactive atmosphere occurs with gases which are introduced into the coating chamber through a valve.

Different evaporation sources can be used to evaporate coating materials. They must satisfy the following requirements:

- The vapour pressure of the material used to construct the evaporation source must be so low at the evaporation temperature that it does not contaminate the coating to be deposited.
- The coating material may not form an alloy, a chemical compound or a eutectic mixture with a low melting point with the evaporation source material, as otherwise the source will be destroyed.
- The evaporation source must have a geometric form which allows defect-free coating with the relevant coating material.

For the materials used to coat flat glass, the evaporation sources, also called evaporators, are mainly of tungsten in the form of a filament or wire, which act as electrical resistance heaters. Common forms of the filaments used are shown in Figure 4.2.2.3.2.

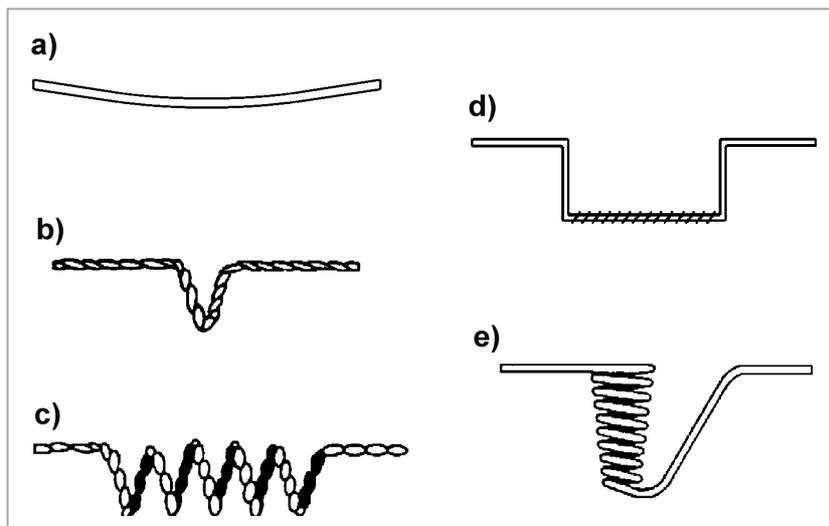


Figure 4.2.2.3.2 Forms of evaporators for coating flat glass by thermal evaporation

- a) wire-formed evaporator
- b) hairpin-formed evaporator
- c) spiral-formed evaporator
- d) wire-formed evaporator with embossed winding path
- e) basket-formed evaporator

The evaporators (a) to (d) are used to evaporate gold, silver, copper, aluminium or metal alloys such as nickel chrome in the form of wire. Source (e) is used for materials such as zinc sulphide and silicon oxide in the form of pills, tablets or granulate. Wires of the coating material are hung within the evaporator (b) and (c). Wires of the coating material are wound around the evaporator wire of (a) and (d). The coating material is positioned within the evaporator of form (e). Considerable experience is needed to know which evaporator

form is optimal under which conditions for which application. However, decades of experience with thermal evaporation have been described in the relevant literature (e.g. Kienel/Frey, Haefer in the references). The batch-mode systems used today to coat flat glass by thermal evaporation usually operate quantitatively, i.e. the amount of coating material introduced into the sources is determined by weighing before each coating process.

Occasionally resistance-heated crucibles are used or electron guns, which heat the coating material with an electron beam. As this evaporation technology is no longer used for coating flat glass, these methods will not be described further here. Instead, the reader is referred to the relevant literature (e.g. Kienel/Frey).

In all cases described here, the evaporators act effectively as point sources, i.e. the material to be evaporated spreads out from a single point in the vacuum chamber and condenses on the substrate.

Figure 4.2.2.3.3 shows the distribution of the evaporating material and its deposition on two parallel flat glass panes positioned at equal distances from the source for this case.

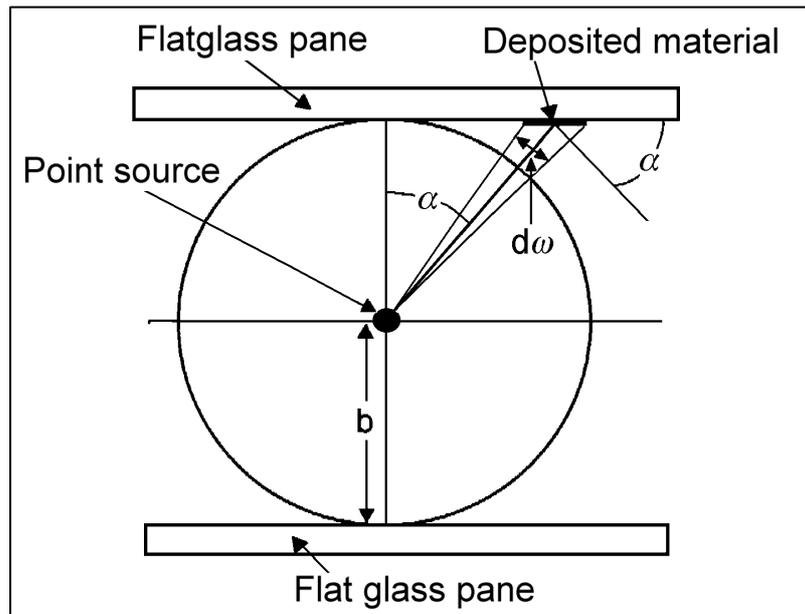


Figure 4.2.2.3.3 Distribution of the evaporated material vapour from a point source and its deposition on two parallel flat glass panes positioned at equal distances from the source

From this figure, it is easy to understand that the amount of material dm evaporating per unit of time dt into the solid angle $d\omega$ on the glass surface decreases with the cosine of the angle α to the surface normal through the point source. Formally, the following equation applies:

$$\frac{dm}{dt * d\omega} = \frac{\Theta_0}{4\pi} * \cos \alpha$$

where Θ_0 is the total amount of material evaporating from the point source per unit of time. From this equation, it is theoretically obvious that uniformly thick coatings can be prepared only across a very limited area from a point source.

In the batch systems which operate today with thermal evaporation for large-area coating of flat glass, several point sources above and adjacent to each other in a so-called evaporator field are used. The number of point sources depends on the pane area to be coated.

Figure 4.2.2.3.4 shows the design of a coating arrangement for the thermal evaporation of large-area flat glass panes existing of two vertically mounted panes with an evaporator field centrally positioned between them.

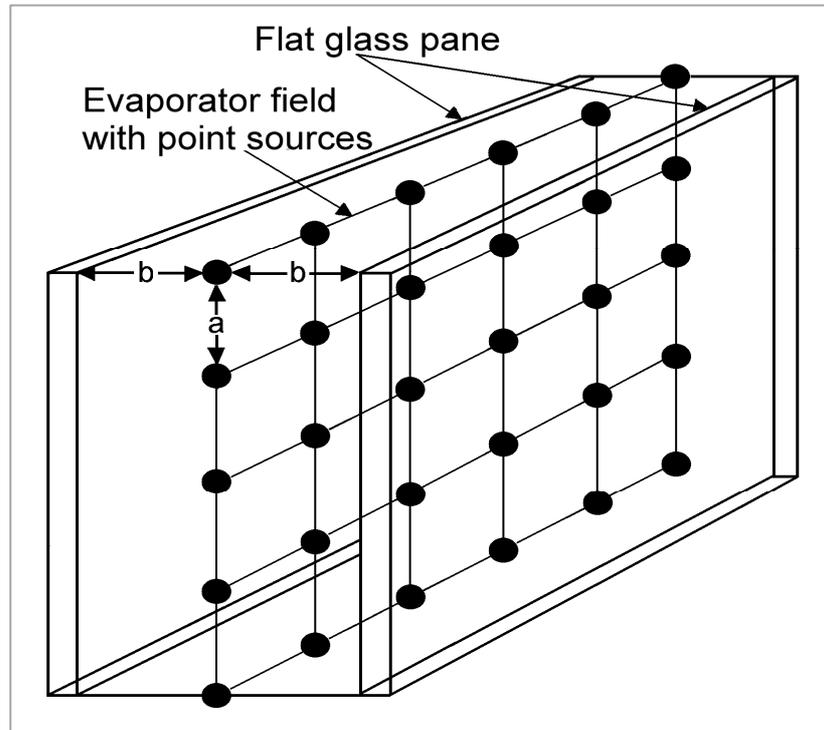


Figure 4.2.2.3.4 Diagram of the configuration of the evaporator field and the panes to be coated by static thermal evaporation

Due to the angular dependence of the material flux for thermal evaporation from point sources, as described above, it is theoretically not possible to deposit uniformly thick films on large-area panes from an evaporator field consisting of point sources. Theoretically, it is only possible to achieve approximately uniformly thick coatings with this technology by optimising the evaporator distances **a** and the distance to the panes **b**.

However, in practice it has been found that adequate uniformity of the coating thickness can be achieved during thermal evaporation with point sources by optimising

- the pressure during evaporation and
- the speed of the evaporation process, i.e. the evaporation rate.

In the first case, the direction of the vapour flux is homogenised by scattering from residual gas particles in the vacuum chamber and in the second case, surface diffusion causes a uniform distribution of the vapour particles incident on the panes. Both approaches demand considerable experience. However, practical application has proven that it is possible to deposit interference coating stacks without visible colour deviation with the point sources presented here, when they are arranged in an evaporator field as shown in Figure

4.2.2.3.4 . This indicates that the large-area deviations in coating thickness are only a few nanometres.

It has become evident that the number of evaporators in the evaporator field near the pane edges can be minimised if the point sources in the evaporator field are positioned as shown in Figure 4.2.2.3.5.

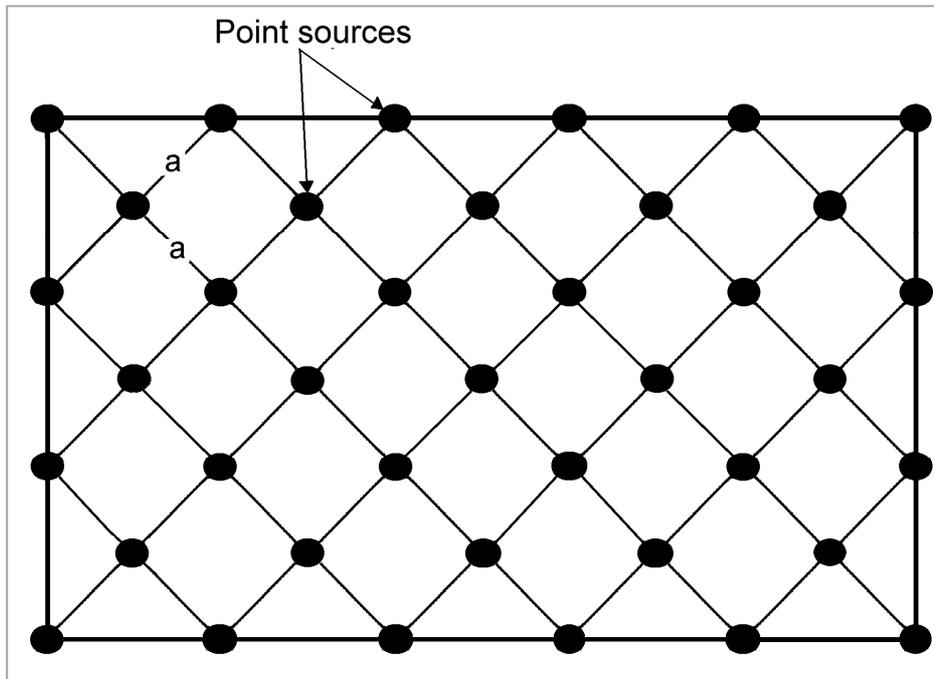


Figure 4.2.2.3.5 Positioning of the point-source evaporators in an evaporator field for industrial coating of flat glass panes

The batch systems with thermal evaporation which are still used today operate in a static coating mode, i.e. the panes and an evaporator remain fixed relative to each other during evaporation. Dynamic coating with lines of evaporation sources, which remain fixed while the panes to be coated are transported along them, was also applied in combination with two in-line facilities in the past, similarly arranged as is usual for sputtering today (see Chapter 4.2.1.7). However, they have not established themselves in industrial production.

4.2.2.4 Coating plants and processes applying thermal evaporation

Figure 4.2.2.4.1 depicts the design of a single-chamber plant for coating large-area flat glass panes by thermal evaporation in batch operation, which was developed by the Heraeus company in Hanau, Germany at the beginning of the 1960's and is still used in this form today. A static coating mode is applied, i.e. flat glass panes are mounted vertically on fixed supporting frames at an equal distance to both sides of an evaporator field within the coating chamber. The evaporator field consists of evaporation sources analogous to those shown in Figure 4.2.2.3.2. The vacuum is created with a high-vacuum pump. Inert gases or air enter the chamber via a gas inlet diametrically opposite the vacuum pump flange during the glowing process or evaporation itself if required. Electricity to heat the sources is supplied by low-voltage power supplies. The plants have three evaporators per evaporator position, as shown in Figure 4.2.2.4.2, which can be loaded with different coating materials.

Thus stacks of multi-layers can be deposited by switching over the power supplies during the coating process to the different loaded sources.

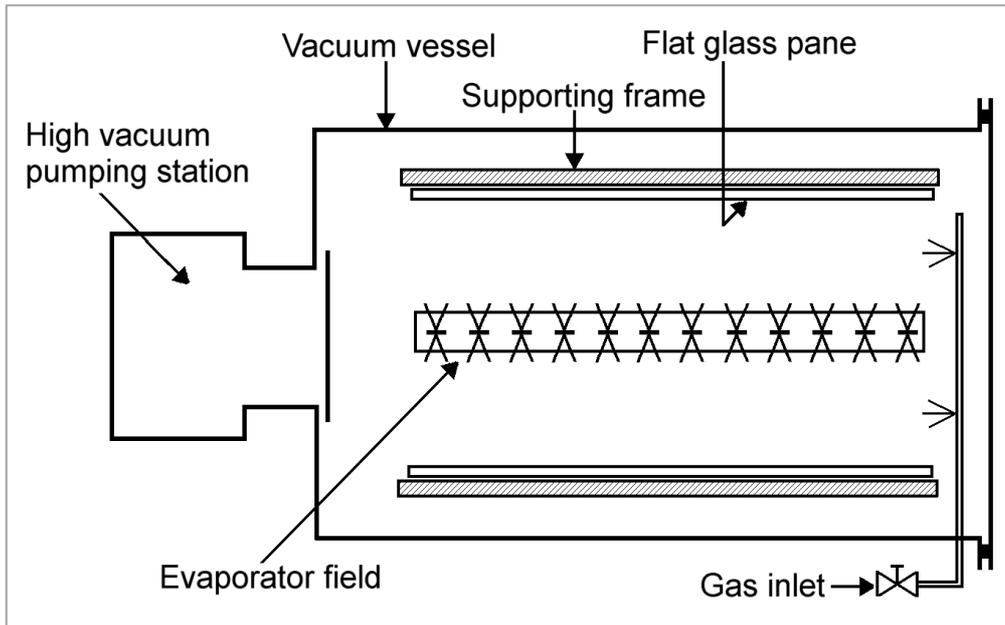


Figure 4.2.2.4.1 Diagram of the Heraeus plant to coat large-area flat-glass panes by thermal evaporation

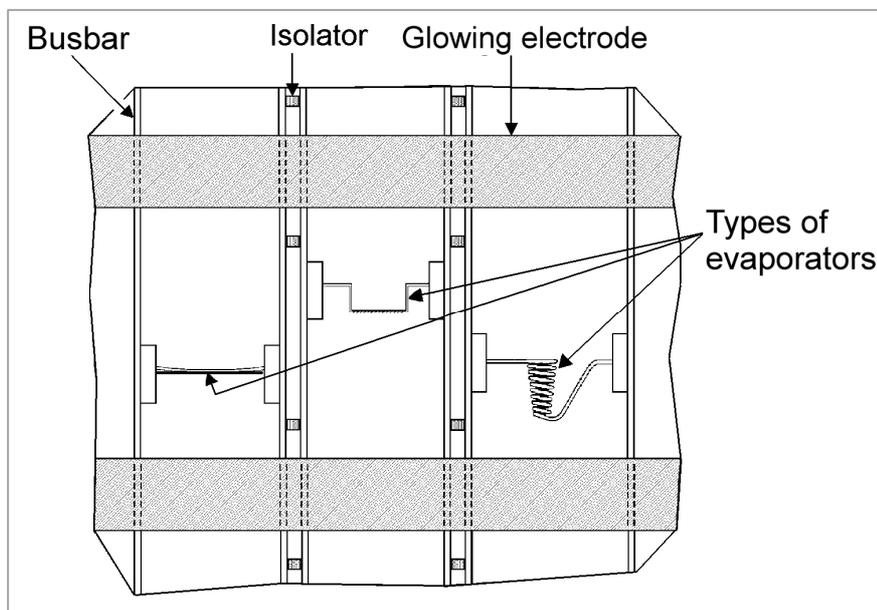


Figure 4.2.2.4.2 Diagram of the arrangement of the evaporation sources in the Heraeus plant

The three sources for evaporating different materials are positioned parallel to each other in a plane at the evaporator position. Rail-formed electrodes for the glowing process are mounted above and below the evaporator position. The distance **a** between the evaporator positions is about 50 cm; the distance **b** between the evaporators and the glass panes is about 60 cm.

The evaporator configuration shown in Fig. 4.2.2.4.2 can also be used to evaporate more than three single layers. If the evaporation rates of the materials to be deposit vary strongly

with the evaporation temperature, a single evaporator can be used to evaporate two materials by first evaporating one material with a correspondingly high vapour pressure at low temperature and then evaporating the other material with a correspondingly high vapour pressure at high temperature. This method is also called 'fractional evaporation'.

Figure 4.2.2.4.3 shows a schematic time-dependent pressure profile during thermal evaporation with the Heraeus plant to deposit a three-layer coating on a large-area flat glass, e.g. with the composition zinc sulphide/gold/zinc sulphide.

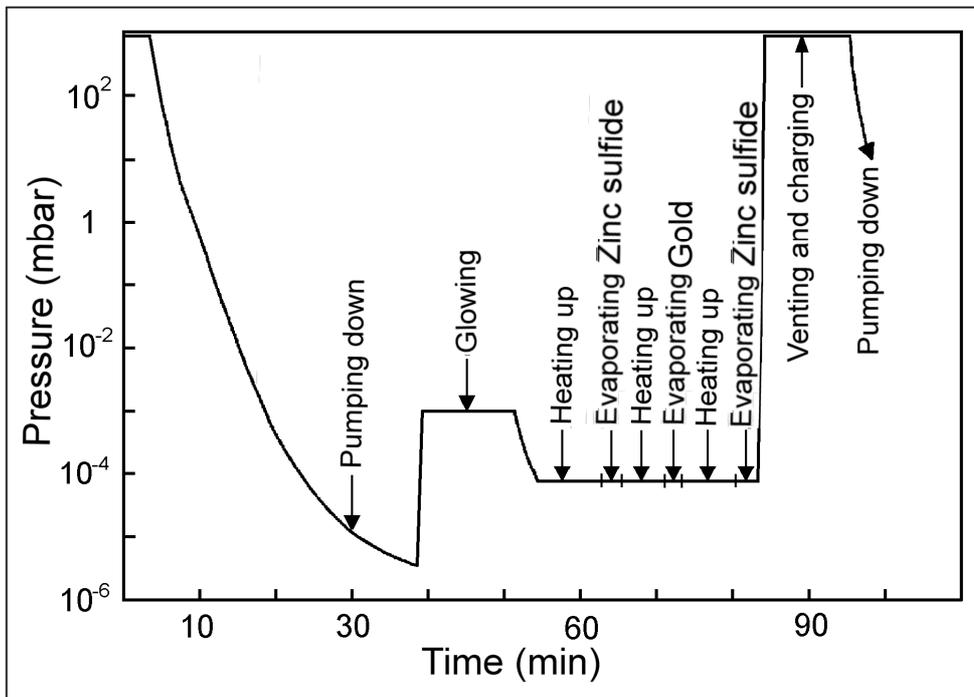


Figure 4.2.2.4.3 Time-dependent pressure profile for depositing of a three-layer coating with the Heraeus thermal evaporation plant

After the glass panes, mounted on the supporting frames, and the evaporator field have been positioned in the coating chamber, it is evacuated to a pressure of app. 10^{-6} mbar. Then gas (air or argon) is admitted to a pressure of app. 10^{-2} mbar for the substrate cleaning by glowing, for which 2 kV is applied for about 15 minutes. Then the chamber is pumped down again to 10^{-6} mbar and air or argon is introduced until the evaporation pressure of e.g. $8 \cdot 10^{-5}$ mbar is reached. Subsequently, the evaporators for depositing the first layer are slowly heated for 5 to 10 minutes until they reach evaporation temperature, after which the coating material slowly evaporates for several minutes. By switching the power supply to the corresponding evaporators, the same procedure is repeated to deposit the other layers. After coating, the vacuum chamber is opened and prepared for the next batch by removing the supporting frames with the coated glass panes and the depleted evaporator field from the chamber.

The required uniformity in coating thickness can be achieved by a suitable choice of the distance **b** between the panes and the evaporator field, an appropriate charging of the individual evaporators, a suitable pressure for evaporation and an appropriate rate of heating the evaporator sources. From the number of parameters to be optimised, it is obvious that considerable experience is needed to coat large-area flat glass panes by thermal evaporation.

The Heraeus plant including its supporting frame carriage is illustrated in Figure 4.2.2.4.4. Flat-glass panes with dimensions of up to 2.40 m x 3.40 m, i.e. maximum 40 m²/batch, can be coated in such a plant. Its coating capacity with three shifts a day amounts to 50,000 m²/a.



Figure 4.2.2.4.4

Photo of the Heraeus plant
(source: Vegla, Aachen, Germany)

It is still used today to manufacture solar-control coatings and occasionally special multi-layer coatings on flat glass. The advantages of this plant are that a great variety of coatings can be produced in small batches and also that bent glass panes with a pitch of up to about 30 cm can be coated. However, the disadvantage of this plant is the large manual effort needed to weigh the coating material for each source and to load the 177 sources in the evaporator field for each coating batch. In addition, considerable maintenance is needed for these plants, as the coating material, which accumulates during each coating process on the interior wall of the coating chamber and acts like a sponge for gases, must be removed by sand-blasting from time to time. Otherwise, the required low pressure would no longer be reached when the chamber is evacuated. The material flow in coating by thermal evaporation is analogous to that for sputtering with batch facilities (see Figure 4.2.1.7.5).

The two in-line evaporation plants for coating large-area flat glass, that were mentioned above, have not been reproduced and will be presented only briefly in the following paragraphs. The interested reader is referred to the relevant literature (see Schiller and Grubb in the reference list).

The production scheme for one of the two plants, which was designed by the von Ardenne Institute in Dresden at the end of the 1960's, is shown in Figure 4.2.2.4.5. The panes to be coated, with dimensions of up to 1.80 m x 2.20 m, are stacked horizontally in an entrance magazine. Then the whole plant is pumped down to high-vacuum pressures. In order for

the multi-layer coating to be deposited, the panes were individually transported horizontally through the coating chamber across three successively positioned evaporator arrays and were subsequently stacked in an exit magazine. The evaporator lines were equipped with electrically heated crucibles. After coating was completed, the whole plant was vented. While the exit magazine with the coated panes was unloaded, the entrance magazine was loaded for the next charge. The plant was mainly used to deposit solar-control coatings based on silicon oxide/copper/silicon oxide onto glass. The coating capacity of the plant is specified to be 10,000 to 100,000 m²/a.

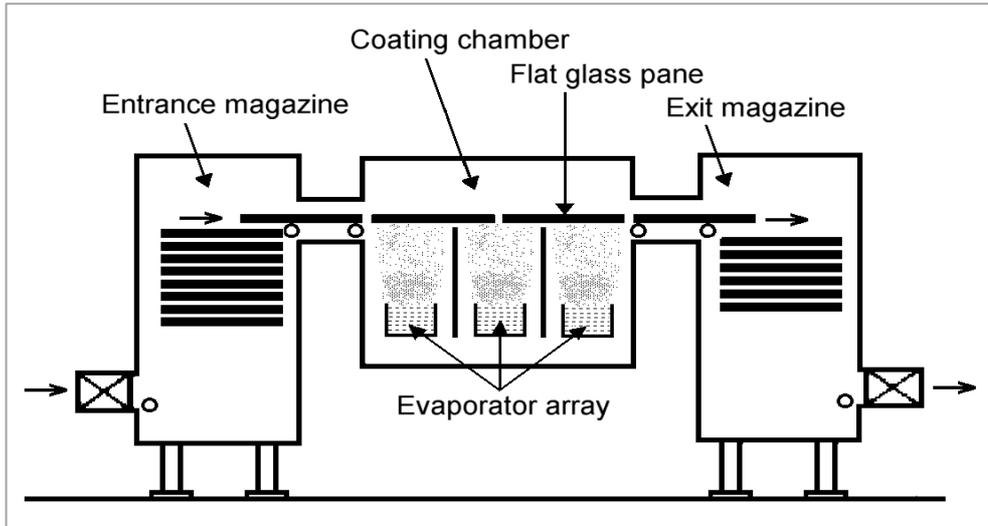


Figure 4.2.2.4.5 Production scheme of the von Ardenne plant for coating flat glass with solar-control films by dynamically thermal evaporation (source: Schiller)

The second in-line plant for coating large-area glass panes by dynamically thermal evaporation was designed by the Airco company, USA and operated for several years by the LOF company, also in the USA. Its flowchart for the production process is illustrated in Figure 4.2.2.4.6.

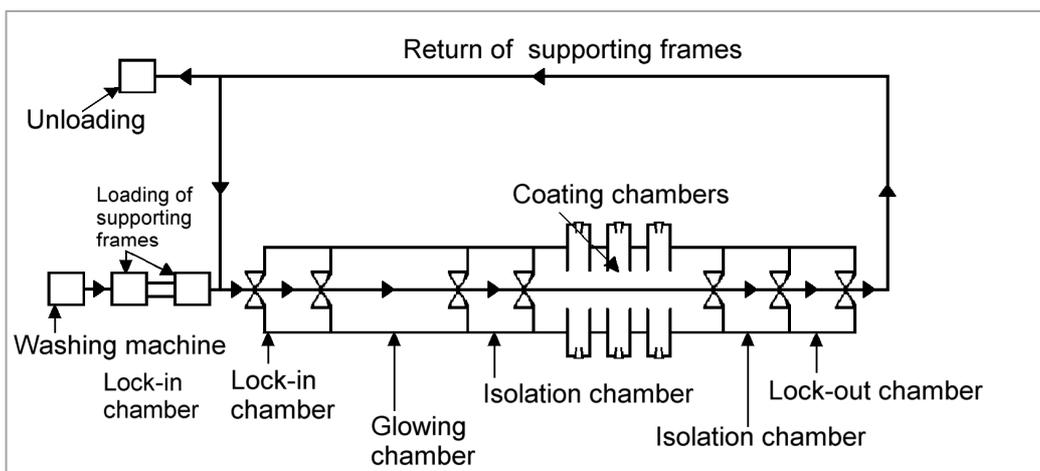


Figure 4.2.2.4.6 Flowchart of the production process with the LOF plant for dynamically thermal evaporation of solar-control coatings on flat glass (source A. Grubb)

This coating plant works analogous to modern in-line sputtering plants (see Figure 4.2.1.7.2.5). In this case, however, the panes were mounted vertically on supporting frames and introduced to the coating chamber via an air-lock chamber; similarly, an air-lock chamber was used for their exit to the atmosphere after coating. The coating chamber was equipped on both sides with three evaporator lines, each with four evaporators, whereby each evaporator was heated with three electron beam guns and electric power of 50 kW. In this fashion, solar-control coatings with up to three individual layers, essentially based on chromium and chromium oxide, could be deposited on panes with dimensions of up to 120 in. x 144 in. (3.05 m x 3.56 m). Both the design and operation of the plant were very complicated. In the community, it was known as the “Jolly Monster”.

4.3 Chemical processes employed for flat glass coating

There are a number of chemical coatings and coating processes in use today. They all have in common the fact that the layer is deposited during a chemical reaction on the substrate surface. The individual processes are distinguished by the ambient pressure at which the reaction takes place, either at atmospheric pressure or at low pressure, i.e. under vacuum. Today, mainly atmospheric-pressure reactions are employed to coat large area flat glass panes. These processes are collectively referred to as APCVD (atmospheric pressure chemical vapour deposition). For some years, attempts have also been made to use plasma-assisted chemical processes to coat large area flat glass panes. These processes can be classified as chemical processes (chemical deposition - CD) and vacuum processes (physical vapour deposition - PVD) (described in Chapter 4.2). Chapter 4.4 will be devoted to the plasma-assisted chemical processes.

Because the chemical reactions of several materials form the basis of chemical deposition, it is obvious that the coating processes have to be adapted to the characteristics of these reactions. The following processes are applied for flat glass coating today:

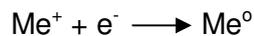
- **Chemical reduction**, also known as ‘electroless plating’, where metals are reduced from a compound with the help of a co-reactant to form a layer on the substrate surface; this process will be discussed in Chapter 4.3.1
- **Chemical reaction on a hot substrate surface**, where the coating material reacts with a certain reactant (e.g. air, oxygen, steam) to form an oxide layer. Processes applying this technique are described in Chapter 4.3.2. If the coating material is a liquid substance the liquid spray deposition technique is preferred. If the coating material is a gaseous substance (or an evaporated liquid), the chemical vapour deposition technique (CVD) is used. Finally, if the coating material is in powder form, the powder spray deposition technique can be utilised.
- **Sol-gel deposition**, where the substrate surface is covered with a dissolved metallic-organic compound, the sol, which is then transformed into a gel by hydrolysis achieved by water or humidity. After this step the gel is densified at high temperatures and transformed into to a solid metal oxide layer. The most important coating technique in the sol-gel deposition for flat glass panes is dip-coating. For some future applications, the flow technique is also suggested. Chapter 4.3.3 describes sol-gel deposition

4.3.1 The chemical reduction process

Chemical reduction is probably the oldest known method of flat glass coating. It has been employed to manufacture silver mirrors since the middle of the 19th century. Today more than 100 million m² of silver mirrors per year are produced world-wide by this method. This is why it is of greatest importance for flat glass coating, ranking second after sputtering among all the coating techniques, in terms of quantity. Until a few years ago transparent solar control layers for solar control glass were also made on a commercial scale by means of chemical reduction technologies. However, other coating technologies, particularly sputtering (see Chapter 4.2.1) and chemical coating of the hot flat glass surface (see Chapter 4.3.2), have replaced this method. Coating by means of chemical reduction is always carried out off-line, i.e. independently of the flat glass manufacturing process.

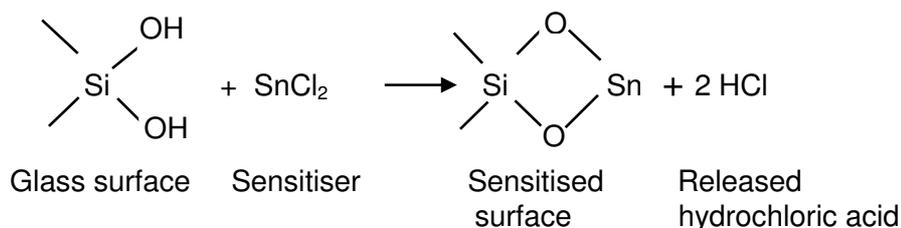
4.3.1.1 Chemistry of coating by means of chemical reduction

Reduction basically means ions or atoms taking up electrons, as opposed to oxidation, where ions or atoms release electrons. When chemical reduction reaction is used for a coating process, dissolved metal ions (Me⁺) are applied together with a reducing agent which delivers electrons (e⁻) to the Me⁺ ions. Unlike galvanic coating processes, this electrical neutralisation takes place without the influence of an electric current. The basic equation for reduction is therefore:



where Me⁰ is a neutral metal atom. It is important to note that the reduction does not take place homogeneously in the entire volume of the solution, but on the surfaces of solids, provided that these act as catalysts. Therefore chemical reduction is often also referred to as 'catalytic reduction'. Electrically conductive surfaces of solids act as catalysts. If the metal atoms are deposited on to these surfaces they generate another catalytic surface so that the reduction process of Me⁺ ions can continue. This process is called 'auto-catalysis'. Auto-catalysis allows layers of any thickness to be deposited uniformly on to substrate surfaces.

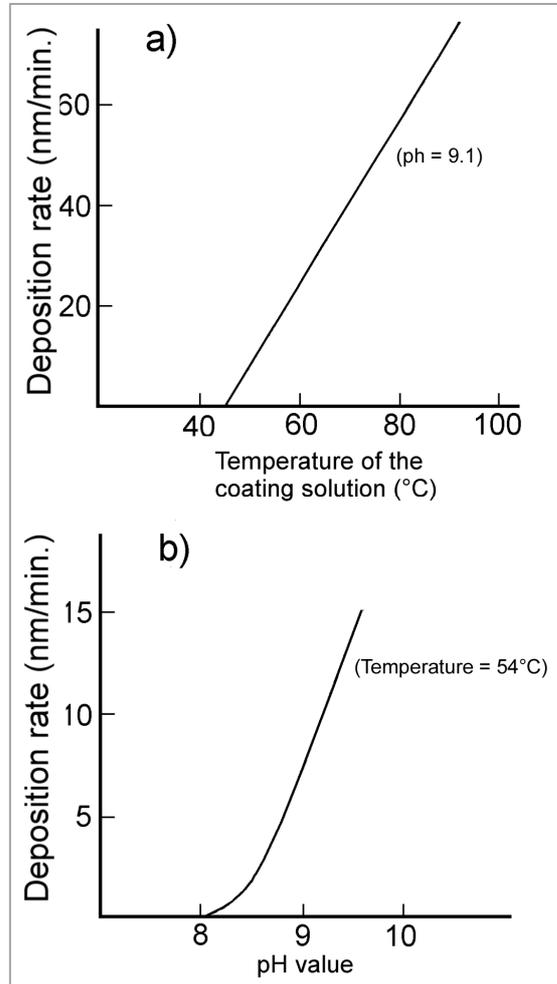
In order to coat non-conductive and hence non-catalytic substrate surfaces, such as glass panes, with metallic layers the surface must first be sensitised for catalysis. This can be done by spraying the surface with a palladium dichloride (PdCl₂) or a tin dichloride (SnCl₂) solution. Today, the latter material is the one predominantly used; the sensitisation can be de-scribed chemically as follows:



According to this equation, the sensitisation results in tin ions (Sn²⁺) being deposited on to the flat glass pane which becomes electrically conductive as a result of the subsequent reaction with metal ions, i.e. then it acts as a catalyst for a further deposition of metal atoms.

The deposition speed of the metals, also called the deposition rate, which corresponds to the geometric sputtering rate R_d (see Chapter 4.2.1.3), depends on the temperature of the solution containing the coating material and its pH value. Figure 4.3.1.1 shows this with the example of the deposition of a nickel-cobalt layer on to a sensitised glass surface.

Figure 4.3.1.1
Coating rates of nickel-cobalt layers on a sensitised glass surface
a) as a function of the temperature of the coating solution for a constant pH value
b) as a function of the pH value of the coating solution for a constant temperature
(source: Campbell)



It is important to ensure that not only the substrate temperature but also the solution temperature and pH value are adjusted so that an adequate deposition rate can be achieved on the one hand and the layers are as uniformly thick as possible on the other.

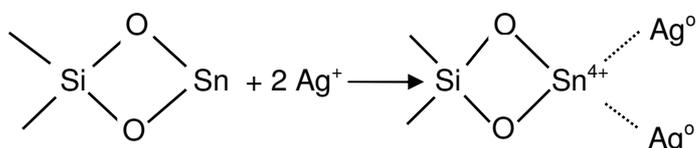
A number of metals can be coated by means of chemical reduction, e.g. copper, nickel, cobalt, iron, silver, palladium and platinum as well as alloys consisting of these metals. The following reducing agents are used with them:

- Sodium hypophosphite for nickel and cobalt
- Sodium borohydride for nickel and gold
- Dimethylamine borane for nickel, cobalt, gold, copper and silver
- Diamide for nickel, gold and palladium
- Formaldehyde and glucose for copper and silver

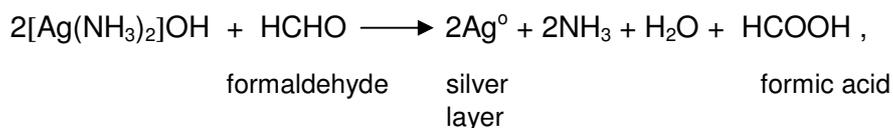
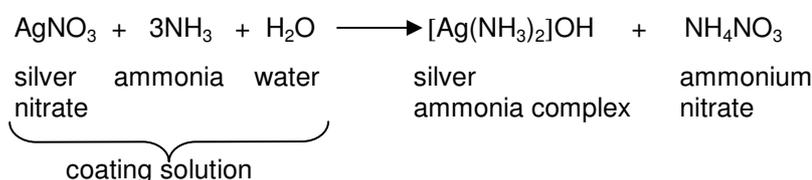
All the above-mentioned metals can be deposited on to flat glass surfaces as long as these have been sensitised first. Only silver mirrors are produced on a commercial scale today using the chemical reduction process.

In order to prevent the silver layer from corrosion, until a few years ago it used to be covered with another copper layer coated by the same process. Today, copper layers are increasingly being replaced by tin lacquer coatings, also deposited by the same process. The coating of these coatings appears to be less harmful to the environment and is more economic. The design of the layer system was previously laid out in DIN 1238 (see Chapter 5.4.1, Part II); however, the current European standard EN 1036 concerning glass mirrors no longer contains regulations about layer design.

The silver coating process for mirror manufacturing is carried out as follows: After the preparatory sensitisation stage the panes are pre-silvered with a silver solution which contains no reducing agent. Ag^+ ions are added to the terminal Sn^{2+} ions and so reduced to neutral silver (Ag^0) by the tin ions, which, in turn, are oxidised to Sn^{4+} . The pre-silvering step can be described as:



During this pre-silvering stage the flat glass surface becomes electrically conductive so that the auto-catalytic silver coating can start, for example, with ammoniacal silver nitrate solution and formaldehyde as the reducing agent, according to the following chemical reactions:

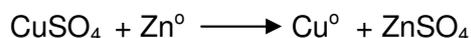


Since this cannot be seen easily in the equation it must be added that it becomes possible for the silver ions (Ag^+) to be reduced to metallic silver (Ag^0) because of the free electrons which are released by the oxidation of formaldehyde to produce formic acid. The pH value of the silver solution has to be set in the alkali range, i.e. above 7, for the coating process.

During the dehydration of the emerging complex silver ammonia compound, explosive silver fulminate $[\text{Ag}(\text{NH}_3)_2]\text{O}$ may be deposited on the walls of the prepared ammoniacal silver nitrate solution container. Silver fulminate is a highly explosive substance which has repeatedly led to accidents. Therefore, alkali-free complex silver compound solutions are predominantly used for the silver mirror manufacturing process today. Gluconic acid is then used, for instance, as the reducing agent, as compounds of this do not harbour the risk of explosions. Moreover, such improved substances have the advantage that the reaction time of the reduction processes is very short, which permits higher deposition rates and hence

enables economical production with high capacity coating plants for an output of several million square metres of mirrors per year.

The subsequent copper plating, if it is applied, is previously carried out using a watery zinc powder suspension and a copper sulphate solution through the direct contact process, according to the equation:



The copper layer (Cu^0) is deposited according to this equation because of the general chemical rule which states that base metals (in this case zinc) precipitate the more precious metal copper from its salt, which corresponds to a reduction of copper and an oxidation of zinc. However, this contact process has the disadvantage that the side effect of releasing hydrogen makes it difficult to deposit strongly adhering thick films, which are necessary to protect the silver layer mechanically. This disadvantage can be avoided by using complex copper solutions in the disproportionation process for the copper-plating stage. This process makes use of the property of dissolved monovalent copper (Cu^+) ions that one part is reduced to metallic copper (Cu^0) and the other part is oxidised to bivalent copper ions (Cu^{2+}) in a 50:50 ratio. The equation for the disproportionation process is:



The advantage of the disproportionation process is that it allows copper layers of any thickness to be deposited. However, it is expensive to dispose of the waste copper solutions which arise in this process. The materials in the last years used for manufacturing mirrors have the advantage that the reaction times of the reduction processes are very short, such that high coating rates are possible, as are needed for an industrial coating plant with a production capacity of several million square metres per year. In addition, the coating process with these coating materials is safe to operate.

However, as mentioned above, instead using copper as protection coating of mirror manufacturing different other protection coatings are applied today, e.g. tin or even lacquer coatings. They are ecologically less harmful and, as reported, they have the same protective functions just as the copper coating. In addition, they reduce the costs for the silver mirror manufacturing.

4.3.1.2 Coating techniques using the chemical reduction process

In the past, two major chemical reduction techniques were used for the manufacturing of silver mirrors: the pouring method and the tilting method, the former being the oldest. For the pouring technique, the panes to be coated are laid horizontally on heated tables and the coating solution is poured on to the pane surface together with the reducing agent, resulting in deposition of a silver layer. The excess solution is then poured off. The procedure is repeated until the desired thickness for the silver layer is reached. However, it is now some time since this technique has been in use, unlike the tilting technique, which has continued to be used occasionally until recently. For the latter, the panes to be coated are placed into a centrally-suspended, tiltable shallow tank into which the coating solution is poured, together with the reducing agent. The solution wets the pane surface uniformly as the tank is tilted, which leads to a uniform thickness of the silver layer. Both the pouring and tilting method are

manual techniques which are not suitable for production on a commercial scale with current demands.

The coating method used almost exclusively today is the spraying technique. The solutions containing the metal compounds and the reducing agents, which are prepared, stored and applied separately, are pumped into spray guns with which the solutions are sprayed onto the previously sensitised pane surface using compressed air. The layer is generated immediately or just after the liquids strike the substrate. It is very important to avoid the coating solution being reduced on the way from the guns to the flat glass pane, otherwise the layer homogeneity is noticeably impaired. The silver and the protective layer of copper or tin are coated one after the other in separate chambers and the excess liquid is washed away with demineralised water and re-processed. After the protective layer has been deposited the dual layer system is dried by radiant heat and finally coated with a lacquer (see Chapter 5.4.1; Part II). The entire coating of silver mirrors today is carried out as an in-line process.

Figure 4.3.1.2.1 shows the diagram of a modern in-line mirror silvering plant.

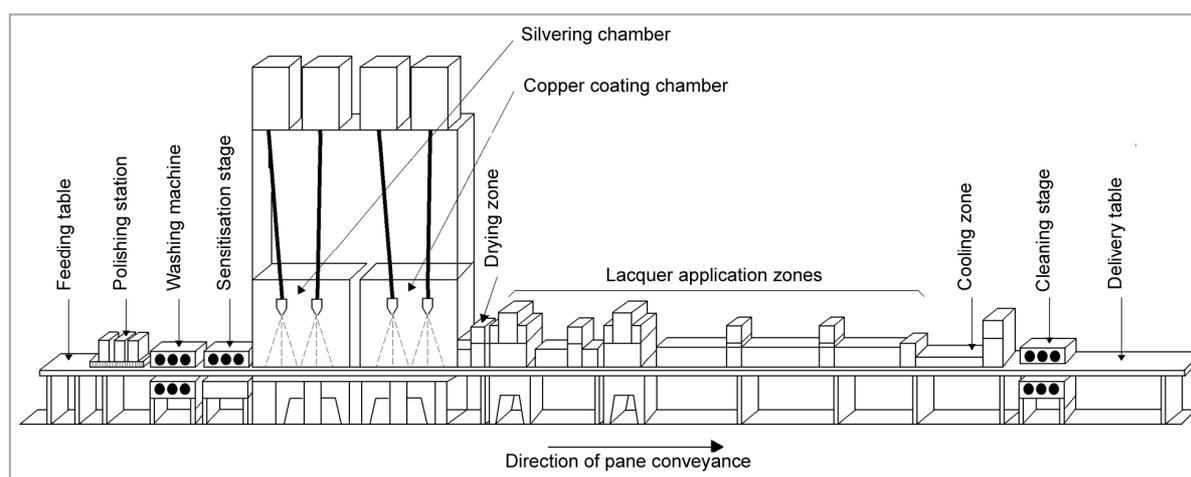


Figure 4.3.1.2.1 Diagram of a modern in-line silvering plant for silver mirrors

Viewed in the direction of the production course, this modern plant consists of a feeding table and a scrubbing/ polishing station, which is followed by a washing machine. The next stage is the sensitisation station where tin dichloride is applied and, after the required reaction time, washed off again, all by means of spray guns which are operated using compressed air. The next stages are the coating chambers, first the silvering chamber and then the copper or tin coating chamber. Then the dual metallic layer system is stabilised in a drying zone before it is painted to protect it from corrosion effects and mechanical damage. Two lacquer paints are applied: a primer and a top lacquer (see Chapter 5.4.1, Part II). After that, the panes pass through a cooling zone and a cleaning stage. Finally, a stacking device lifts the panes from the conveyor belt and stacks them for dispatch.

In-line silvering plants have a length of approximately 200 m. They are capable of processing jumbo size panes, i.e. panes with dimensions of up to 3.21 m x 6.00 m. Usually, the conveying speed is 8 m/min, from which an annual coating capacity of up to 2.5 million m² can be calculated. Certain prerequisites must be fulfilled to operate successfully a modern silvering plant. First, the flat glass panes must meet strict quality standards (see Chapter 3.2.3), i.e. the pane surface must be free of corrosion, since the deposition of a uniformly thick layer is not otherwise possible, resulting in mirrors with faulty coatings. To ensure high

quality, the panes undergo a scrubbing/ polishing stage before they are washed. Polishing agents such as cerium oxide or Jeweller's Rouge are used in a disc brush stage to remove potential corrosion. Secondly, the coating solutions must react quickly on the pane surface. The silvering solutions (metallic solution and reducing solution) used today ensure this, so long as they are sprayed separately. The reduction process is initiated spontaneously when the sprayed solutions reach the pane surface. Figure 4.3.1.2.2 shows the spraying equipment inside the coating chamber of a modern silvering plant. The spray guns for the metallic and reducing solution are arranged alternately in a row. The array of the gun rows oscillate perpendicularly to the direction of pane conveyance.

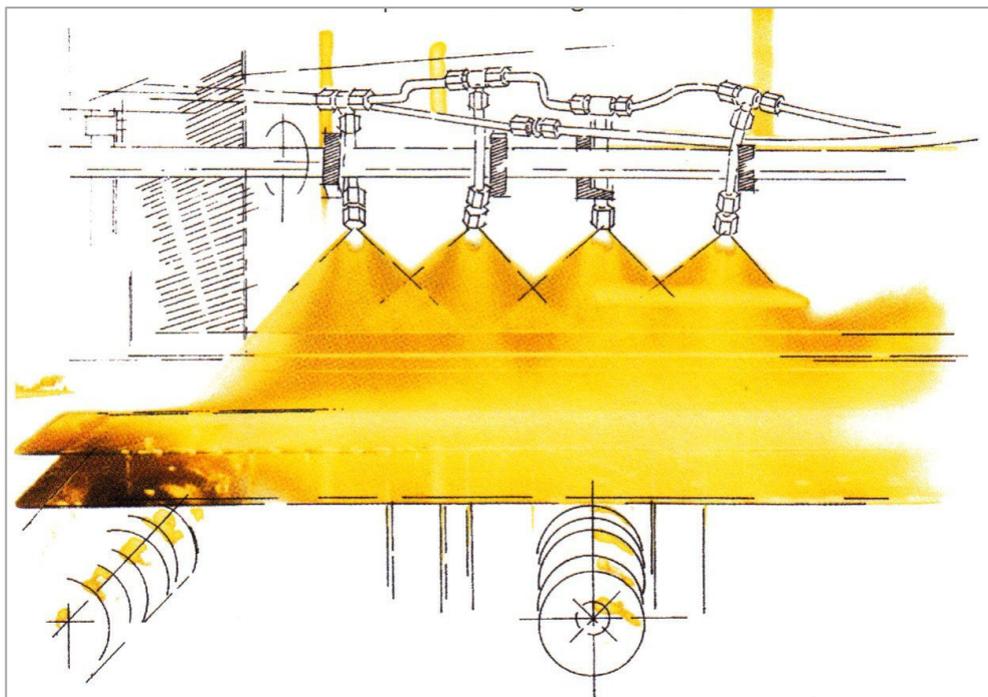


Figure 4.3.1.2.2 Diagram of spraying equipment for coating solutions in a modern mirror silvering plant

To operate a modern in-line silvering plant, a large amount of demineralised water is needed, the continuous supply of which was not feasible until the 1940s. Then industrial-type water decalcification equipments based on ion exchangers were introduced, allowing the operation of in-line silvering plants for mirror production. Furthermore, the panes must be heated and cooled smoothly and with extreme caution when drying the cover lacquers, otherwise the panes are likely to warp, which can make it impossible to transport them through the plant. Modern convection ovens are capable of doing this so that even jumbo size panes can be coated today using the process described above.

In the 1960s, transparent solar-control layers for solar-control glass (see Chapter 5.2, Part II) were also deposited with chemical reduction technology in the USA and in Europe. The companies PPG (USA), Glaverbel (Belgium) and Emmaboda (Sweden) have coated panes with solar control layers on the basis of copper, nickel, cobalt and iron or alloys of these metals, and gold by means of reduction of the corresponding compound salt solutions. Solar control glass coated using this process has a limited light transmittance of maximum 20 %. However, such coating types are replaced by other coating processes and since disappeared from the market.

Layers coated with the chemical reduction process do have some disadvantages in solar control glass applications. First, semi-transparent layers, i.e. with a transmittance of about 50 % in the visible range, cannot be deposited with a uniform thickness. They have a cloudy appearance when looked through. This defect can partly be overcome by depositing thicker layers. However, this has the effect of lowering the transmittance to such an extent that the panes no longer meet the requirements for application as solar control glass, especially in Europe. Secondly, coating processes on the basis of chemical reduction do not allow the deposition of transparent anti-reflection layers in-line, as is often required for solar control glass, for colour design reasons. These may be significant explanations for the fact that solar control glass with coatings produced by the chemical reduction process has disappeared from the market.

Due to the lacking uniformity of the coating thickness caused by the chemical reduction process, more material must be deposited for silver mirrors to attain the spectral light reflectance ρ of 83 % specified by EN 1036 than for uniformly deposited coatings (see also Chapter 5.4.1, Part II). Another disadvantage of the chemical reduction process is that it results in solutions containing metals as waste products, which are expensive in post-processing and/or disposal. But, it is reported that the chemical reduction process still remains the most economical way to produce silver mirrors (see details in Chapter 5.4, Part II). Recently, however, mirrors on the basis of an aluminium coating should be reborn again manufactured by magnetron sputtering processes replacing the silver mirror on the market.

4.3.2 Chemical coatings on hot flat glass

Chemical coatings on hot glass surfaces have been carried out since the late 19th century. It has been recorded that at that time decorative interference effects were already being generated by this process with tin oxide layers. In the 1930s, this method was used by GEFFCKEN et al. from the Schott & Genossen company in order to coat small glass surfaces such as spectacle-lenses. This coating method was then called the 'gas decomposition process'. Only after the Second World War did flat glass begin to be coated using this technique.

It is a common requirement of all chemical coatings on hot flat glass surfaces that heat is needed for the chemical reaction. It is therefore only logical to combine these processes on-line with the production of flat glass or tempered safety glass (TSG) so that the heat of the glass ribbon during flat glass production or the glass panes during TSG production can be utilised as process heat for the coating stage. This is why, in the past, it was mainly at flat glass works and by manufacturers of tempered safety glass that such coating processes were operated. Today, chemical coating on hot flat glass surfaces is carried out almost exclusively by flat glass works in conjunction with the float glass production process.

The chemical coating process is employed for the deposition of non-selective solar control coatings (see Chapter 5.2, Part II), electrically conductive layers on the basis of $\text{SnO}_2\text{:F}$, as used for low emissivity layers and conductive glass (see Chapters 5.1.2.1, 5.1.3 and 8, Part II). In the past, attempts were also made to substitute silver mirrors with dielectric (non-metallic) mirror layers by applying this process (see Chapter 5.4.2, Part II). On a smaller scale, electrically conductive and hence low-emissivity SnO_2 layers were and still are coated off-line using such a process, e.g. for oven doors and heatable refrigerator or heat shields in

fire doors. In the hollow glassware industry SnO₂ coatings are often used to increase mechanical strength, i.e. to toughen bottles. By means of very thin SnO₂ layers, applied by chemical coating on hot bottles, micro-flaws in the glass surface (see Chapter 1.4.2) can be sealed, such that the comparatively high residual local stress is reduced, improving resistance to tensile stress. Similarly, thin SnO₂ layers can be used to increase the limited tensile strength of flat glass. However, to achieve this, the coatings must be applied to both surfaces.

All layers applied on hot flat glass surfaces by means of chemical reaction have high mechanical and chemical durability, comparable to uncoated flat glass. In fact, the treated surfaces often exhibit even better values. Furthermore, these layers display extremely good adherence to the flat glass surface, because they are bonded to it by Si-O-Me bridges.

Despite the considerable efforts of flat glass works in the development of the process over the last few decades, chemical coatings on hot flat glass surfaces have not yet gained the economic importance of sputtering processes (see Chapter 4.2).

4.3.2.1 Chemical reactions of coatings on hot flat glass surfaces

During chemical coating of hot flat glass surfaces, coating materials dissolved in an organic or inorganic solvent or as a vapour or powder and dispersed in a carrier gas such as air, nitrogen or argon are supplied to these surfaces at temperatures from about 500 to 700°C, i.e. after the forming process of the flat glass. There it reacts with the surrounding atmosphere and/ or with the oxygen of the flat glass surface, generating an oxide layer on to it. If the coating material is conveyed on to the pane by means of a solvent, the latter either evaporates immediately before or upon arrival on the hot glass surface, or otherwise acts as an agent in the layer-generating chemical process.

For chemical coating on hot flat glass, a number of gaseous, liquid and solid coating materials can be used. The materials used today and the corresponding chemical reactions of the coating processes can be classified into the following groups:

1. Metal salts which, dissolved in water and applied in a gaseous or vaporous condition, react with the hot flat glass surface according to the reaction



where Me is a bivalent metal ion, X a monovalent halogen, e.g. chlorine, and HX is an acid. Acid, e.g. hydrochloric acid (HCl), which is released during the process, is indicated by an upward arrow (↑) in the equation. The indices (solid, liquid, vapour or gaseous) indicate the state of aggregation of the reactant or reaction product.

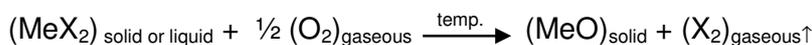
2. Metal-organic compounds which decompose on contact with the hot flat glass surface and generate a layer by reaction with oxygen from the surrounding atmosphere or from the pane surface, according to the reaction



where Me is also a bivalent metal ion, R is an organic radical, i.e. a residual organic molecule, e.g. an acetyl acetate, and x, y and z are the number of involved molecules. Carbon dioxide (CO₂) and water vapour (H₂O) are released during this process.

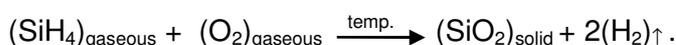
Alternatively, metal-organic compounds with the general formula $\text{Me}_n\text{X}_x\text{R}_{n-x}$ are used as coating materials, where n indicates the valence of the metal ion. Dimethyl tin dichloride is an example of such a substance.

3. Metal salts which decompose on contact with the hot flat glass surface and generate a layer by reaction with oxygen from the surrounding atmosphere or from the pane surface, according to the reaction

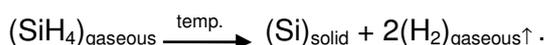


where Me is a bivalent metal ion and X a halogen. The halogen is released during the process.

4. Silane (SiH_4) which decomposes on contact with the hot flat glass surface and generates an SiO_2 layer by reaction with oxygen from the surrounding atmosphere or from the glass surface, with hydrogen released, according to the reaction



If the process is controlled in such a way that the silane cannot react with oxygen, elemental silicon is deposited according to the reaction



The coating processes according to reactions 1 to 4 above are carried out at pane temperatures of 500°C to 700°C . If the coating material arrives at the flat glass surface in solid state, e.g. if the solvent has previously evaporated, the material has to sublime (i.e. evaporate) on contact with the hot surface in order to achieve a uniform layer. The coating material vapour then reacts with reactants on the flat glass surface generating a coating. To manufacture optically faultless layers it is further necessary to remove completely all gaseous and vaporous substances which are released during the reaction.

The layers have a high level of adherence to the flat glass surface because, during the layer formation, there is also a chemical reaction of the coating material with the flat glass surface, resulting from bonds by Si-O-Me bridges. Moreover, the layers themselves are usually chemically and mechanically very resistant (see Chapter 4.3.2).

All coating materials should meet the following requirements:

- Chemical stability and suitability for storage for a defined period before application
- Availability in a gaseous, liquid or vapour state, if necessary, they must be easily transformed into a vapour state
- Non-flammability and non-toxicity
- Deposition rate must correspond to the application technique
- Ability to form a uniform coating on large-area flat glass panes
- Gaseous or vaporous substances arising from the chemical reactions should be harmless to the environment and easy to dispose of
- Low cost compared to the achievable price of the final product so that the entire process can be run economically

No coating material fulfils all these requirements completely. It is therefore necessary to find a compromise regarding coating material and application technique for the coating needed.

Because the coating processes discussed here are operated at temperatures of 500°C to 700°C, it must be noted that diffusion can occur on the interface between glass and coated layer. In the case of flat glass coating, it can be observed that (mainly) sodium ions from the glass body diffuse into the coating layer, thereby 'polluting' it right through to its outer surface, thus influencing its properties and functions. If metal chlorides are used as coating materials, it is even possible that common salt (NaCl) particles are precipitated within the layer. These salt particles form scattering centres for incident light which is the cause for the diffuse scattering of light, the notorious 'haze'. The precipitation of such salt scattering centres is typical in the case of SnO₂ and In₂O₃ layers formed on the basis of their chlorides. The phenomenon of sodium diffusion is effectively retarded in practice by using interfacial diffusion-blocking layers (also known as interface barrier layers) with which the flat glass panes are coated prior to the deposition of the functional layers.

Coating processes on flat glass must ensure a high level of uniformity regarding layer thickness and optical properties, such as the refractive index. Not only must the coating material be applied on to the pane surface extremely evenly, the released reaction products and excessive coating material must also be consistently removed from the surface. All systems for coating on hot flat glass surfaces are therefore not only equipped with deposition equipments, e.g. spray guns, but also with suitable suction equipments and, in some cases, quite expensive treatment plants to remove waste substances, the latter in order to comply with environmentally governmental regulations.

In the following chapter, the major application methods will be discussed which are or were employed for chemically coating large-area flat glass panes: the liquid spray, CVD and powder spray deposition techniques.

4.3.2.2 Technological processes for chemical coating of hot, large-area flat glass panes

Coating with the liquid spray technique

The liquid spray technique was first used by the firm PPG (USA) in the late 1940s for the chemical coating process on hot, large area flat glass surfaces. The product 'LHR' (Light and Heat-Reflecting) was one of the first solar-control coatings made off-line using this technique; the product 'Nesa' was the first electrically conductive glass product, being coated with a transparent, electrically conductive tin oxide layer applied by liquid spraying. Coating with the liquid spray technique was then developed further as an on-line technique in combination with the flat glass production process.

For some years, the liquid spray technique has been replaced in flat-glass coating applications by the chemical vapour deposition (CVD) technique, which is also used on-line in conjunction with flat glass production (see below). An essential reason for this transition is that coatings of higher quality can be produced with CVD technology. For this reason, liquid spraying should be treated here only briefly.

Figure 4.3.2.2.1 shows the principle of equipment to apply the liquid spray technique for chemical coating of hot flat glass. From the diagram, it can be seen that the heated coating solution is mixed with a carrier gas in a dispersing unit in a controlled manner. The dispersed solution is then applied onto the hot flat glass surface through spray nozzles. While the panes are transported below the spray nozzles, the nozzles oscillate perpendicularly to the direction of conveyance above the pane spraying the coating solution in the same way as for mirror coating (see Figure 4.3.1.2.2), but in this case onto the hot glass surface. In this type of equipment, metal salts dissolved in water or organic solvents, or metal-organic compounds dissolved in suitable solvents, can be applied. They then react on the pane surface according to the chemical reactions 1 - 3 in Chapter 4.3.2.1. Air is generally used as the carrier gas.

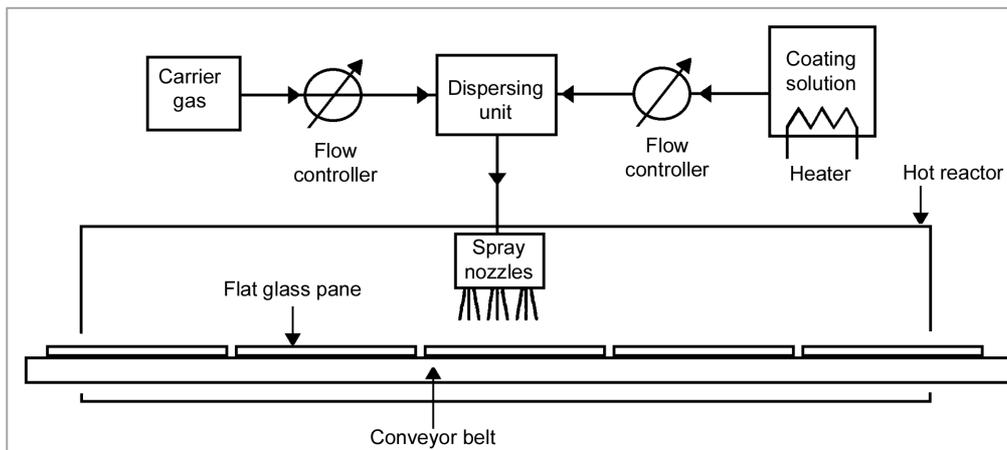


Figure 4.3.2.2.1 Schematic diagram of an equipment for coating hot flat glass by the liquid spray technique.

The coating system in combination with float glass production is positioned at the exit of the tin bath and immediately before the glass ribbon enters the cooling zone, as shown in Figure 4.3.2.2.2. The glass ribbon has a temperature of approximately 600°C at this position.

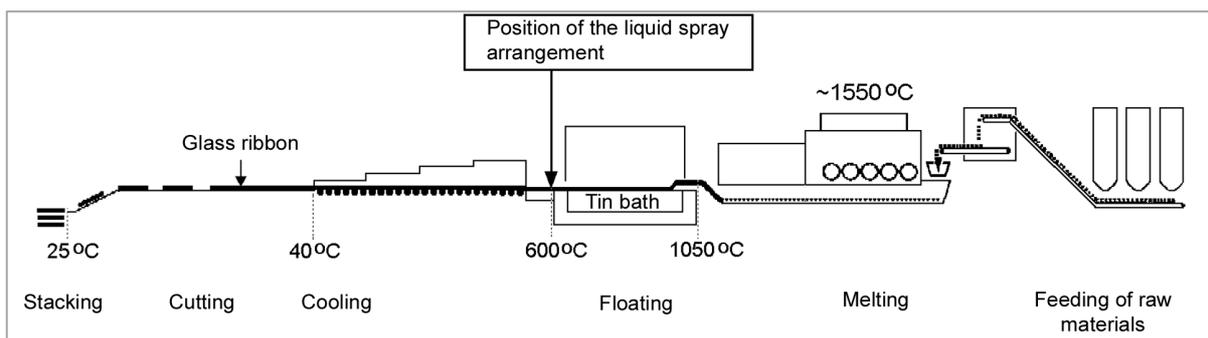


Figure 4.3.2.2.2 Position of the liquid spraying equipment within the flat glass production line.

This on-line coating process on hot flat glass was used to deposit non-selective solar control layers, predominantly those based on cobalt-iron-nickel mixed oxides or titanium oxide on panes with dimensions of up to 3.21 m x 6.00 m (see Chapter 5.2, Part II). 'Solarcool' (PPG, USA), 'Stopsol' (Glaverbel, Belgium), 'Antelio' and 'Parello' (St. Gobain, France) and 'Reflite' (Nippon Sheet, Japan) were or still are brands – even if the coatings are produced by CVD process today – of solar-control glass that have coatings of these oxides. The thermally insulating, low-e-coated panes such as 'Sungate 500' (PPG, USA) and 'Comfort' (Glaverbel,

Belgium) were initially also coated by liquid spraying on-line within the glass production process.

The advantage of liquid-sprayed coatings as compared to coatings produced with PVD (i.e. sputtering or thermal evaporation) that they are mechanically and chemically extremely stable, and thus weather-resistant. The panes can thus be installed with the coating on the outdoor glazing surface (position 1, as it is known in the trade; see more in the Chapter 5.1.3.1, Part II).

The disadvantages of the liquid-spray coating technique are that the nozzles used for spraying are effectively point sources and the spraying liquid is deposited as droplets. Both aspects act against uniform deposition of the coatings, which is essential to achieve colour uniformity in semi-transparent coatings such as solar-control and low-e coatings, particularly when the glazing is viewed from outdoors. Architectural glazing with lacking colour uniformity is not accepted by the market. These problems are greatly reduced when CVD coatings are used. For this reason, once the CVD process had become sufficiently established for coating of large-area flat glass, the production of several of the branded products named above was transferred to CVD and the trademark was retained.

Coating with the CVD technique

Whereas with the liquid spray technique, as described in the previous section, the coating materials transported to the hot flat glass surface are in a liquid state, the CVD technique requires gaseous or vaporous materials. The chemical reactions on the hot flat glass surface that lead to coating deposition may be identical with both methods.

The CVD technique is not as old as the liquid spray technique. It has been used since the early 1960s, when monocrystalline layers were applied to produce semi-conductor components. Figure 4.3.2.2.3 shows a diagram of the chemical coating process from that period, employing the CVD technique to coat hot substrates.

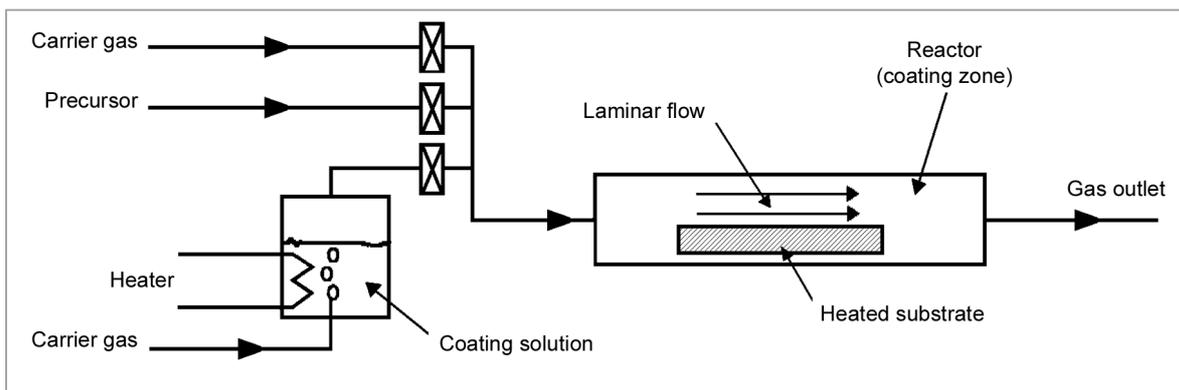


Figure 4.3.2.2.3 Early diagram of coating by the CVD technique

The gaseous or vaporous coating material, also called the 'precursor', glides across the heated substrate with homogeneous, laminar flow guided by a carrier gas, which is at a low pressure of 0.01 to 1 mbar in the case of coating semiconductor elements. The chemical reaction takes place on the substrate surface and a layer is deposited. The deposition rate is usually relatively low in this case.

In the 1970s, attempts were made to apply the CVD technique to large area flat glass panes combined with the float glass production, i.e. as an on-line process. The 'Reflectafloat' solar-control glass (Pilkington, UK) was one of the first products to be coated using this process. In contrast to the production of layers for semi-conductor components, as described above, for flat glass applications the coating gas usually flows at a high speed across the panes at nearly ambient pressure and in a turbulent manner, which allows higher deposition rates and layers with more uniform thickness on large surfaces than those achieved by the liquid spray technique. Apart from this, the process is operated in principle according to Figure 4.3.2.2.3.

The working principle of the CVD technique follows from the laws of fluid mechanics and the chemical reactions before and/ or on the substrate surface. In fluid mechanics, the condition of a liquid, vapour or gas flow is described with the help of the non-dimensional Reynolds number Re . Flows at high velocity are turbulent and have a high Reynolds number, those at low velocity are laminar and have a low Reynolds number. The transitional range from turbulent to laminar flow is specified by the critical Reynolds number, which depends on the geometry of the body through or around which the flow is passed, as well as on the viscosity and the density of the flowing medium. In the case of the application discussed here, the critical Reynolds number should be approximately 2,000.

The chemical reactions of the coating process depend not only on the coating material and substrate surface, but also on how these two may come into contact. For this, the flow condition of the coating material plays an important role. Coating processes with the laminar and turbulent flow of the coating gas or vapour differ in that, in the former case, the deposition rate is determined mainly by diffusion processes from a boundary of the gas/vapour area above the substrate surface, resulting in a rather low deposition rate, while, in the latter case, it is determined mainly by the flow velocity of the coating material towards the substrate, leading to a high deposition rate. In the case of turbulent flow, the flux density j of the coating gas can be calculated as

$$j = p_G \cdot v / k \cdot T$$

where p_G is the partial pressure of the gas/ vapour flow entering the reactor chamber, v its velocity at right angles to the substrate surface, T its absolute temperature and k is the BOLTZMANN constant, a natural constant. From the above equation it follows that the flux density j of the coating gas/ vapour rises with an increasing partial pressure P_G , i.e. the concentration of the gas or vapour particles in the carrier gas, as well as its velocity. Given a turbulent flow and a sufficiently high flux density, the deposition rate R increases exponentially with the absolute temperature of the substrates T_s , according to the equation

$$R \sim \exp(-\Delta E / k \cdot T_s)$$

where ΔE is the reaction energy of the chemical process for the layer formation and k is again the BOLTZMANN constant. According to this equation, the deposition rate is higher, the lower the reaction energy and the higher the substrate temperature.

When coating large-area substrates such as flat glass panes, the coating process carried out with turbulent flows has the great advantage that the coating gas is distributed more evenly over the entire pane surface, leading in turn to an improved homogeneity and uniform thickness of the layer. However, the percentage of coating material which actually reacts on the surface (the coating material yield) is considerably lower than with laminar flows, i.e. the waste is higher.

The coating process for large area flat glass panes, using the CVD technique on-line, i.e. together with the flat glass production process, employs fixed linear nozzles with the flat glass being conveyed under the nozzles. The linear nozzles consist of a slit which covers the entire glass ribbon width (i.e. up to 3.21 m). Figure 4.3.2.2.4 shows the cross-section of a possible design for an on-line flat glass CVD coating arrangement with a slit nozzle.

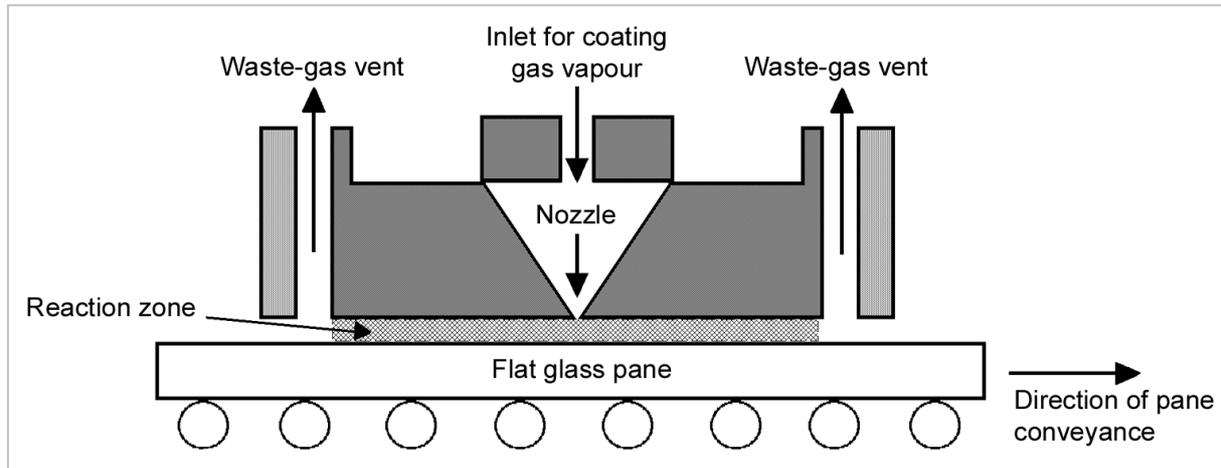
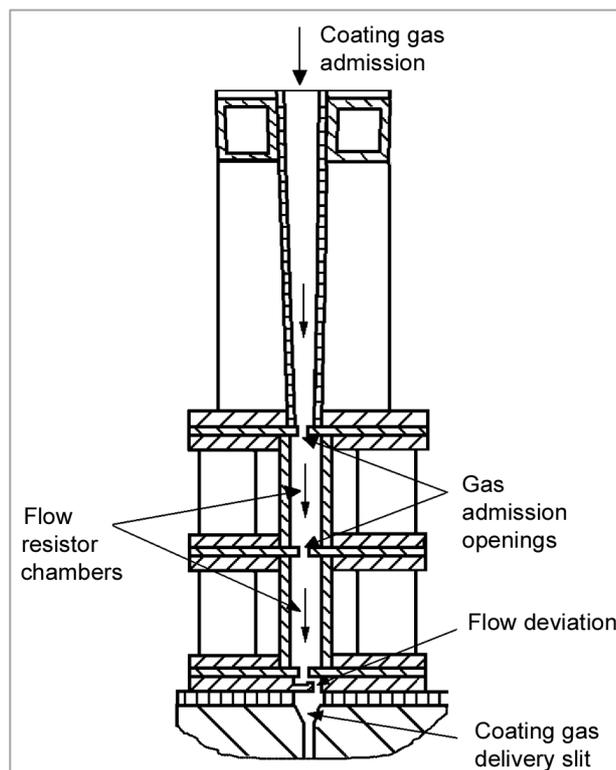


Figure 4.3.2.2.4 Schematic cross-section of a CVD coating equipment for on-line coating of flat glass

Here it can be seen that the gaseous or vaporous coating material and the carrier gas impinge on the glass surface through a slit nozzle in the centre of the equipment and are then conducted to the left and right of the nozzle into the reaction zone across the glass surface with and against the direction of glass ribbon conveyance. The excess coating material and the volatile reaction products are removed through off-gas vents by suction. In other types of CVD coating configurations, the gas mixture is conducted only in the direction of the glass ribbon conveyance and then the waste is again removed by suction.

Figure 4.3.2.2.5

Schematic diagram of a slit nozzle with flow resistor chambers for large-area coating with the CVD technique
(source: EU Patent
0 365 239, Pilkington, UK)

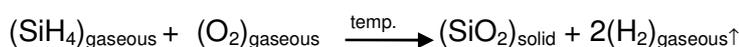


In order to achieve uniform deposition on large area panes, it is further necessary that the gas is admitted at a uniform rate over the entire ribbon width. To ensure this, the gas reaches the slit nozzle through flow resistor chambers, as shown in Figure 4.3.2.2.5, for homogenisation of gas pressure along the slit. Moreover, it is important that the waste gas and volatile materials are also sucked away through the vent at a constant rate.

Coating configurations such as the one shown in Figure 4.3.2.2.4 or similar constructions with only a single-sided reaction zone allow silicon, silicon suboxide (SiO_x) and silicon dioxide (SiO_2) layers to be deposited according to the following reactions (see also Chapter 4.3.2.1):



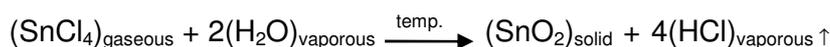
or



The first of these two reactions only takes place sufficiently quickly at temperatures of about 650°C because of the high decomposition energy (known technically as 'sublimation enthalpy') of silane. Predominantly amorphous, silicon containing hydrogen is deposited as a layer. Concerning the second of the two reactions, it should be noted that silane (SiH_4) would already react spontaneously with oxygen at room temperature. However, this would not result in a strongly adhering layer, but rather in a dust-like silicon oxide covering. Therefore, retarding agents are used for the deposition of adhering silicon oxide layers. The gas ethylene (C_2H_6) has proved to be suitable for this. When ethylene is added to the carrier gas, silicon oxide layers can be deposited at temperatures of about 600°C . The oxygen needed for this reaction usually comes from the glass surface, but it can also be added to the carrier gas in the form of carbon dioxide gas (CO_2). In this case, carbidic silicon suboxides with the general chemical formula $\text{SiO}_x(\text{CH}_y)_z$ and a real refractive index n ranging from 1.5 to 2 are deposited dependent on the coating conditions. Such a layer is applied as a sodium diffusion-blocking and also as anti-reflection layer in the case of subsequently deposited tin dioxide layers (see Chapter 5.1.2.1, Part II).

Today, large-area deposition of electrically conductive tin dioxide layers is the most important application of the CVD coating technique incorporated on-line into the float glass production process. The coatings have the formula $\text{SnO}_2:\text{F}$, where F is the fluorine doping which creates the electrical conductivity (see Chapter 5.1.2.1, Part II). For the deposition of $\text{SnO}_2:\text{F}$ layers, dual nozzle arrangements are used with a coating equipment as shown in Figure 4.3.2.2.6.

Here it can be seen that the coating gases for the SnO_2 and the fluorine doping are admitted to the reaction zone separately. The reaction zone has a length of approximately 75 cm. The SnO_2 layer is deposited according to the reaction



According to figures given in the European Patent No.0 365 239, held by Pilkington (UK), the following amounts of material and Reynolds numbers for the coating gases are needed for the on-line deposition of an approximately 320 nm thick $\text{SnO}_2:\text{F}$ layer, with the coating equipment shown in Figure 4.3.2.2.6 at a float glass drawing velocity of 9 m/min marketed with the brand name 'k-Glass' by Pilkington company:

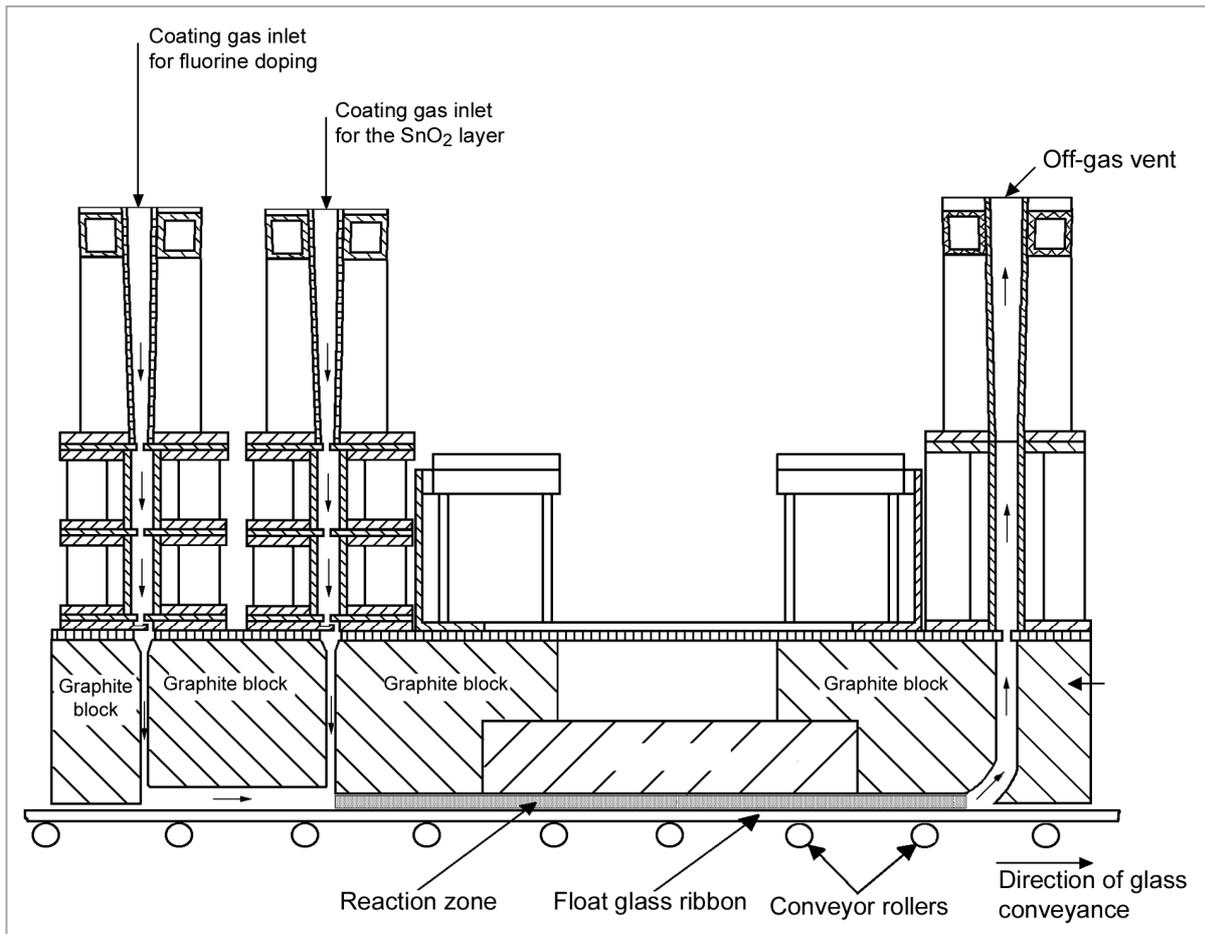


Figure 4.3.2.2.6 Schematic cross-section of an on-line CVD coating equipment to deposit $\text{SnO}_2\text{:F}$ coatings onto float glass

(source: EU Patent 0 365 239, Pilkington UK)

SnCl_4 : 74 kg/h

Dry air: 180 Nm^3/h at 300°C, as carrier and reaction gas

Re: 1,900 at nozzle slit

Coating gas for the fluorine doping, added through the second nozzle:

HF: 35 kg/h

H_2O : 120 kg/h

Air: 576 Nm^3/h at 250°C as carrier gas

Re: 6,100 at nozzle slit exit

Fluorine-doped SnO_2 layers deposited by this CVD process have a light transmittance $\tau > 75\%$ and a sheet resistance R_\square — which is the substantial property for the emissivity (see Chapter 5.1.1.1, Part II) — of about 17 Ω . The Reynolds number $\text{Re} = 6,100$ shows that the gas for the fluorine doping joins the coating gas for the SnO_2 deposition at a very high flow velocity. This is necessary for two reasons: First, the two gases are then mixed thoroughly and secondly, the SnO_2 is highly doped with fluorine, which leads to a low sheet resistance R_\square and thus a low emissivity. The layer is actually deposited on to approx. 600°C hot flat glass surface in the reaction zone at a Reynolds number of the gas mixture of $\text{Re} = 8,100$, i.e. with a high turbulent flow. The resulting deposition rate is about 4 $\mu\text{m}/\text{min}$, which is very

high. However, the yield of tin in the coating gas is only about 8 %, i.e. the vast majority of the coating gas has to be removed from the reaction zone together with the volatile reaction products by the off-gas vent. It is also deposited as solid coverage onto the walls of the coating system, from where it must be removed at regular intervals. Instead of tin tetrachloride (SnCl_4) and hydrofluoric acid, metal-organic tin and fluorine compounds, such as dimethyl tin dichloride $[(\text{SnCl}_2(\text{CH}_3)_2)]$ and trifluoroacetic acid (CF_3COOH), are applicable, as they are chemically less aggressive but more expensive.

During the coating process, some coating material is also deposited within the slit of the coating nozzles, which leads to bottlenecks in the flow of gas especially in the slit of the nozzles. These may result in unevenly thick layers visible as coloured stripes in the direction the float glass is drawn. Furthermore, turbulent gas flows and chemically highly reactive substances, which are added to the process, e.g. hydrofluoric acid, and are produced during it, e.g. hydrochloric acid, result in rapid corrosion and wear of the coating system. The affected parts must therefore be cleaned and replaced periodically, i.e. the equipment requires frequent maintenance.

Figure 4.3.2.2.7 shows possible positions of such CVD coating equipments as part of a float glass production line.

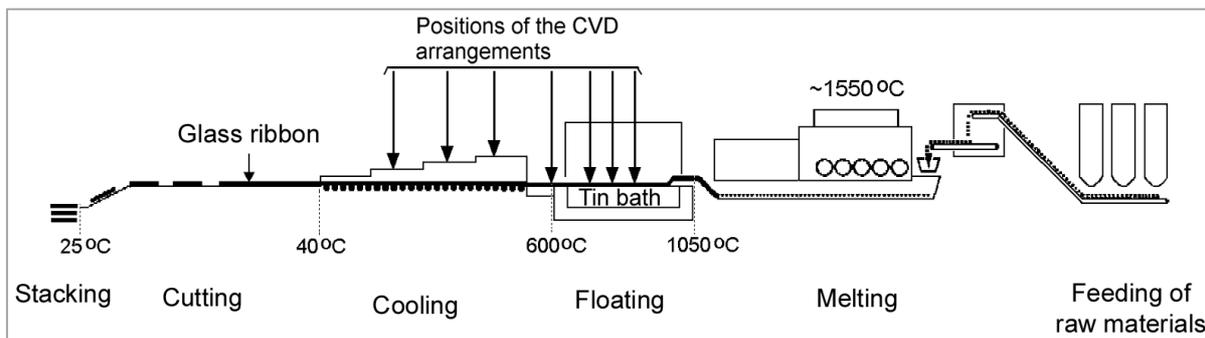


Figure 4.3.2.2.7 Possible positions of the CVD coating equipment incorporated on-line in the float glass production process.

As can be seen from the diagram, the coating equipments can be positioned in the floating zone or in the cooling zone or between the two. Today, silicon, silicon suboxide and silicon dioxide layers are deposited in the floating zone. The $\text{SnO}_2\text{:F}$ layer can also be deposited at this stage, but in most cases it is applied between the floating and the cooling zones.

Compared with the liquid spray technique, the CVD technique has two major advantages, as already described above. Firstly, better uniformity and homogeneity of the layers can be achieved, particularly with layers which are thicker than 100 nm. Secondly, a wider range of coatings can be deposited, especially since the coating equipments can be installed in various positions along the float glass production line. However, the CVD technique has also some disadvantages. The low yield of the coating material is one of them (only 8 %, see above), so that considerable effort is necessary for the disposal or re-processing of the excess coating material and chemically highly aggressive volatile materials and reaction products. Another disadvantage is the rapid attrition of the components of coating equipments which are in contact with the coating material and its reaction products as well as the huge effort required for cleaning, re-processing and replacement them periodically.

Figure 4.3.2.2.8 shows a recycling plant for waste products from the CVD process for the case of on-line $\text{SnO}_2\text{:F}$ deposition.

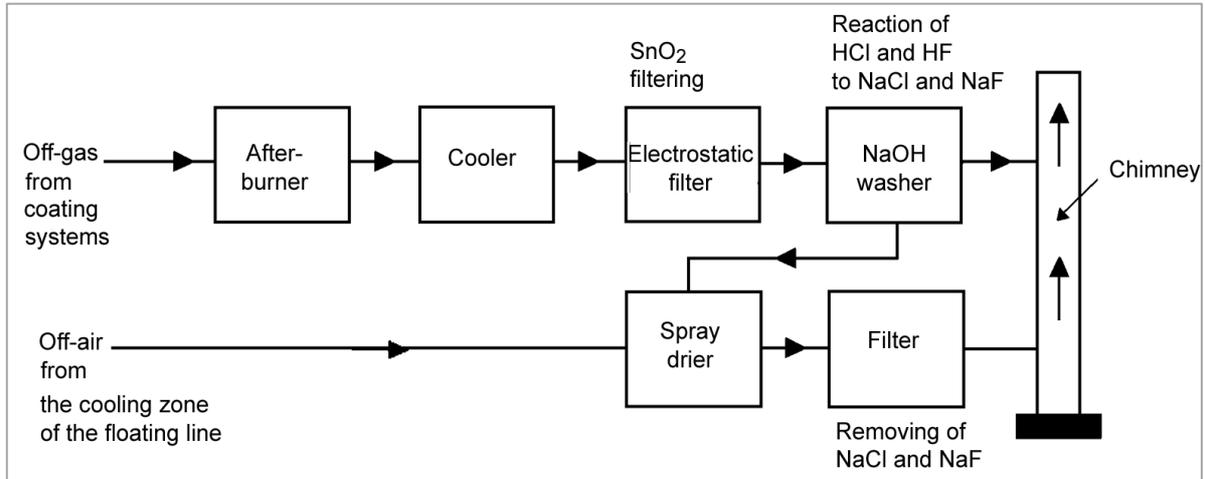


Figure 4.3.2.2.8 Diagram of the recycling plant for the waste gas removed from on-line $\text{SnO}_2\text{:F}$ coating equipment applying the CVD technique

(source: Brochure, GEA, Bochum, Germany)

Recycling plants like these cannot be avoided, because of today's strictly environmental regulations. As shown in Figure 4.3.2.2.8, one might well speak of a 'chemical factory' which follows the CVD coating process. If layer stacks are to be deposited, a similar recycling plant must be installed for each individual layer.

Today, the on-line CVD technique is used throughout the world in conjunction with float glass production. Major products include non-selective solar-control coatings (see Chapter 5.2, Part II) based on metal oxides as described in the section on the liquid spray technique, and low-emissivity coatings (see Chapters 5.1.2.1, 5.1.3.1 and 5.1.3.2) based on $\text{SnO}_2\text{:F}$ with a silicon oxide layer as an intermediate layer. The dimensions of the coated panes are up to 3.21 m x 6.00 m, i.e. "jumbo" sizes. The optical quality, i.e. the freedom from distortion and faults, of the panes coated using the CVD technique meets the acceptance criteria for conventional glazing, as specified in DIN EN 572-2. However, the short-wave planarity of panes coated in this way is not as good as that of uncoated glass (see Chapter 1.2), particularly in the case of thick layers with coating materials where the thermal expansion coefficient is different from that of glass. Panes coated using the on-line CVD technique described above are often not suitable for optoelectronic applications (see Chapter 6.1, Part II).

The hope expressed by promoters of the on-line CVD technique, that it will replace the widespread sputter deposition processes (see Chapter 4.2) for most applications, has not yet been fulfilled. Both techniques will certainly continue to be applied in future, each according to the advantages of the coatings that can be deposited with them.

Thermal powder spray coating technique

The thermal powder spray coating technique was also transferred in the 1970's by a few companies to coat hot float glass on-line as part of the float glass production process. For this technique, the coating material is applied to the hot flat glass as a solid powder. It

decomposes immediately before incidence on the surface; a coating is deposited as a result of reaction with the glass surface and/or the gaseous atmosphere above the surface. The advantage of this technology is that no solvents are required for the coating process. The disadvantages are that not only solvents evaporate during the coating process resulting in extraction of heat from the flat glass, which may then need replacement, but also that some of them are expensive and their disposal is usually difficult. However, the disadvantage of the powder spray coating technique, similar to the liquid spray technique, is that the thickness of the deposited coatings is less uniform than that produced by the CVD technique. This disadvantage, together with the difficulties in managing the coating material, are the main reasons that powder spray coating on hot float glass has not achieved a technical breakthrough. For this reason, only the essential aspects of this technique will be presented in the following section.

Figure 4.3.2.2.9 schematically illustrates the powder spray coating process on hot float glass. The configuration is similar to that for the liquid spray coating technique. Instead of liquids, now the coating material is fed as a coarse-grained powder from a hopper reservoir into a treatment plant, where it is converted to an extremely fine powder with a grain size of several micrometres. From there it is conveyed to a powder distributor, from which it is distributed using dry air as carrier and reaction gas through Venturi or broad slit nozzles onto the float glass surface. Once again, chemical reactions on the hot glass surface result in the deposition of the coating. The coating equipment is located between the floating and cooling zones of the float glass production line, similarly to the equipment for the liquid spray technique (see Figure 4.3.2.2.7).

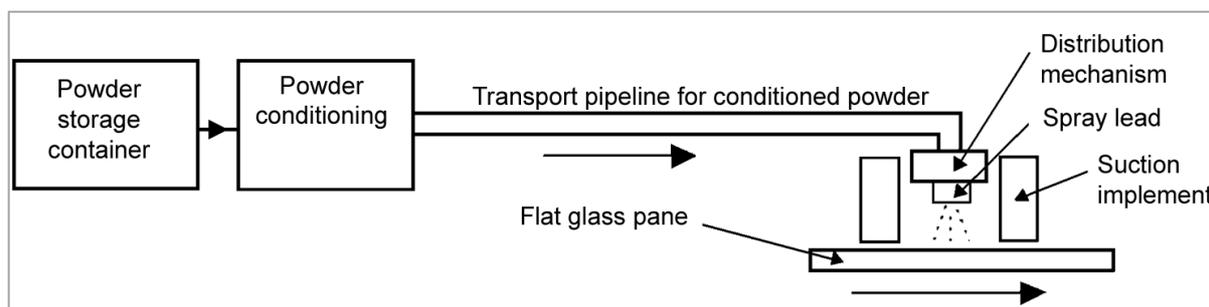


Figure 4.3.2.2.9 Cross-section of the flowchart of thermal powder spray coating equipment for on-line coating of flat glass

The excess coating material and the gases and vapours released during the powder spray coating process must also be carefully removed by suction and subsequently recycled. The necessary effort is the same as for the CVD technique. However, as very fine, dust-like powder tends to react explosively, special protection measures against fire and explosion hazards are necessary.

The thermal spray powder coating technique was used industrially exclusively to deposit oxide films such as electrically conductive tin oxide (SnO_2), cobalt oxide (Co_2O_3), aluminium oxide (Al_2O_3), iron(III) oxide (Fe_2O_3), chromium(III) oxide (Cr_2O_3) and titanium dioxide (TiO_2). Metal-organic powders and metal salts which sublime sufficiently at a temperature of about 600°C and decompose can be used as the coating material. The electrically conductive tin oxide layers ($\text{SnO}_2:\text{F}$) can be produced on a two-component basis with organic tin compounds and addition of hydrofluoric acid or suitable fluorides, as described in the section on CVD coating, or by applying a single-component method based on organic tin fluoride

compounds such as dibutyl tin fluoride, abbreviated DBTF. However, in general it should be noted that, compared to liquid spray coating and the CVD technique, only relatively few materials can be coated by the thermal powder spray technique, which is certainly a disadvantage of this coating technology.

Powder spray coating was used industrially mainly to produce spyhole reflective coatings for vehicle glazing, solar-control coatings for solar-control glazing and low-emissivity coatings based on $\text{SnO}_2\text{:F}$ for thermally insulating glazing. However, these products have now all disappeared from the market.

4.3.3 Sol-gel coating

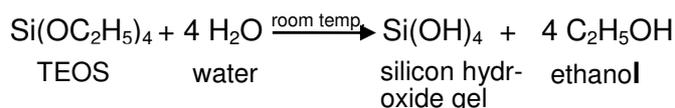
The sol-gel coating process is related to chemical coatings on hot flat glass surfaces (see Chapter 4.3.2). However, the coating procedure is different. This is a technique which enjoys a long tradition. As long ago as the 19th century, attempts were made to manufacture glass synthetically through a chemical reaction, i.e. without the melting process; this was done using a sol-gel process. The sol-gel technique was first applied to flat glass coating by the Schott & Genossen company in the 1930s. Today, it is mainly anti-reflective glass (see Chapter 5.3, Part II) and dielectric mirrors (see Chapter 5.4.2, Part II) which are coated with sol-gel processes. Until several years ago, non-selective solar control glass was also coated with this technique (see Chapter 5.2, Part II).

4.3.3.1 Chemical processes of sol-gel coating

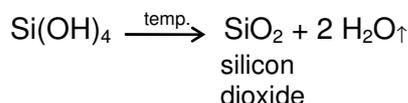
Sol-gel coatings are based on metal-organic compounds, e.g. alkyl oxides with the general chemical formula $\text{Me}(\text{OR})_n$, where Me is the metal component with the valence n and OR is an alkoxy group. The metal-organic compounds, which are dissolved in organic solvents, or more recently also in water, are applied at room temperature to flat glass surfaces, in the form of a liquid film. This film is hydrolysed to a gel film, which is then transformed into a solid metal oxide layer by dehydration at elevated temperatures. The latter procedure is also known as densifying. This means, the *chemical reactions* to deposit a layer with a sol-gel process is a two-stage process and the *coating process* is a three-step process.

As an example, if as coating material tetraethoxysilane (TEOS) may be used for the sol-gel coating process to deposit a silicon dioxide (SiO_2) layer the chemical reaction stages are as follows:

1st reaction stage (hydrolysis)



2nd reaction stage (dehydration, densifying)



The organic solvent in the initial solution and the ethanol released during hydrolysis diffuse out of the emerging gel film and the water used for the gel formation diffuses into it. Afterwards, the gel film is densified in a heat treatment stage, the so-called firing process, whilst water vapour is released.

Today, flat glass can be coated by similar chemical reactions with a number of metal oxides, e.g. titanium dioxide (TiO_2), zirconium dioxide (ZrO_2), tin dioxide (SnO_2), indium oxide (In_2O_3) and aluminium oxide (Al_2O_3), as well as mixed oxides, such as SiO_2 - TiO_2 , and also multi-component oxides such as barium titanate (BaTiO_3).

The actual reactions of the layer-forming process are not as simple as described above. In many cases they are quite complex and have not yet been thoroughly researched. Often they involve a number of intermediate reactions which partly take place in the initial solution and influence the coating process. One of the best-researched sol-gel processes is the SiO_2 coating formation on the basis of TEOS described above, where in fact a larger number of intermediate reactions is involved than shown in the equations.

The long-term stability of the prepared coating solutions forms a significant problem for users of the sol-gel coating technique. In the initial solutions, molecules can tend to agglomerate, which affects the coating process and thereby the quality of the layer. It is true to say that in industrial practice the sol-gel processes succeed or fail with the long-term stability of the coating solutions.

On a commercial scale, it is mainly SiO_2 and TiO_2 , as well as SiO_2 - TiO_2 layers, which are deposited on flat glass by means of sol-gel coating today. These layers are highly resistant to chemical and mechanical attacks and further display an excellent adherence to the flat glass surface, because the coating materials also react with the flat glass surface, resulting in strong bonds between glass surface and layer in the form of Si-O-Me bridges (see also Chapter 4.3.2).

4.3.3.2 Sol-gel coating techniques

As above mentioned, the sol-gel coating process is divided into three main stages:

1. The coating solution is applied to the substrate, i.e. onto the flat glass surface, in the form of a liquid film
2. The liquid film is chemically transformed into a gel film by hydrolysis. During this stage the film absorbs water, usually from humid air, whilst the solvent and possible reaction products are released
3. The gel film is densified to a solid oxide layer by firing it in a furnace at temperatures of up to 500°C

This procedure implies that the sol-gel coating process can only be run off-line, i.e. independently of the glass production process. In order to coat large area flat glass, the dipping technique is predominantly used today. However, several other application methods would also be suitable, e.g. the flow method or the roll-on technique, neither of which have yet been used industrially in the flat glass industry.

The dipping technique

Figure 4.3.3.2.1 shows the three stages of a sol-gel coating process using the dipping technique. In the first stage the pane to be coated is dipped into a bath containing the coating solution (also called the 'dip coater') and slowly drawn out again. Both sides of the glass pane are wetted with a liquid film which is naturally of uniform thickness, because of the surface tension of the liquid. In a specially air-conditioned room, where temperature and humidity are controlled, this film hydrolyses into a gel film. At the same time, solvent and reaction products are released from the film. Finally, the gel film is fired in a furnace at temperatures of approximately 500°C, where an oxide layer is formed by dehydration and densifying.

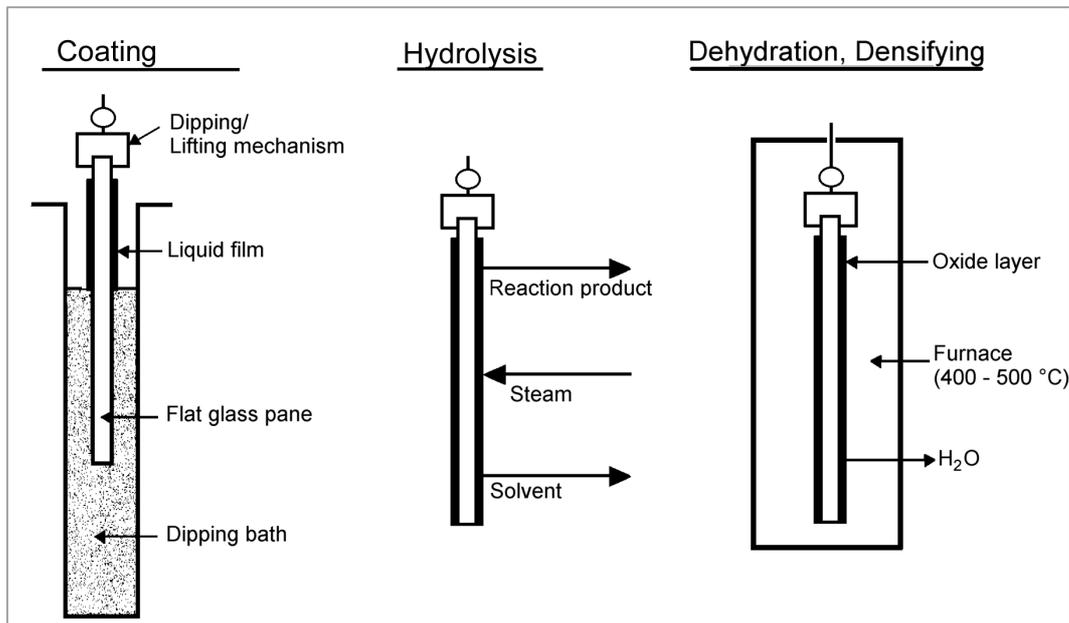


Figure 4.3.3.2.1 Processing stages of sol-gel coating by dipping

The layer thickness is basically determined by adjusting the speed at which the panes are drawn out and/ or the viscosity of the coating solution. The viscosity depends in turn on the temperature and concentration and also on the chemical condition of the coating solution, e.g. on its age (see above). While the first two parameters are adjustable and must be strictly controlled, the ageing of the coating solution is determined by the chemical properties of the metal-organic substance and the solvents which are used. Moreover, the continuous evaporation of the solvent from the dip coater must also be considered when applying the liquid film. Because the dip coaters usually have a capacity of about 2,000 litres and only a small proportion of the solution is consumed during the dipping process, the long-term stability of the dipping solution has a considerable effect on the cost of the sol-gel coating process.

For dip coating the uniformity of the layer thickness depends primarily on the wettability of the flat glass surface. On the one hand, the wetting angle ϕ of the solution against the flat glass must be sufficiently small – in fact ϕ should be as close as possible to 0 (see also Chapter 5.5.1, Part II). On the other hand, the flat glass surface must be perfectly clean and as free from corrosion as possible. To ensure the latter, a labour-intensive preparation of both glass surfaces is required prior to dip coating. For large-area panes, this preparation

process can be divided e.g. into a pre-cleaning stage, an intensive main cleaning stage, which includes the use of chemicals to remove corrosion layers, and a careful surface drying stage, which is performed by infrared radiation (see Chapter 3.4). Moreover, the dip coater must be suspended without vibration and the panes must be drawn out of the dip coater smoothly to guarantee an even layer. The speed at which the panes are drawn out may range between 2 and 15 mm/s. In addition, it is also important that the room atmosphere in which the film is hydrolysed into a gel is not only controlled regarding temperature and humidity, but also that it is kept free of the released organic vapours by means of a laminar air flow. A turbulent flow would have a negative effect on the evenness of the liquid and gel films. The pane thickness has only an insignificant effect on the layer thickness.

To guarantee that the layer be reproducibly fired, the temperature in the furnace must also be carefully controlled during the final process stage. The structure of the layers as well as their thickness and their optical and mechanical properties can be substantially influenced by the tempering process.

The sol-gel process allows layer systems with different metal oxides to be deposited onto flat glass panes. In these cases, the panes to be coated pass through all stages of the coating process several times, each time with a different coating solution in the dip coater. After each dipping process, the individual layers may be dried at lower temperatures, e.g. at 100 to 200°C, and the complete coating stack is then fired at a higher temperature, e.g. at 400 to 500°C.

In Figure 4.3.3.2.2, the individual steps of the sol-gel coating process are summarised in a flow diagram.

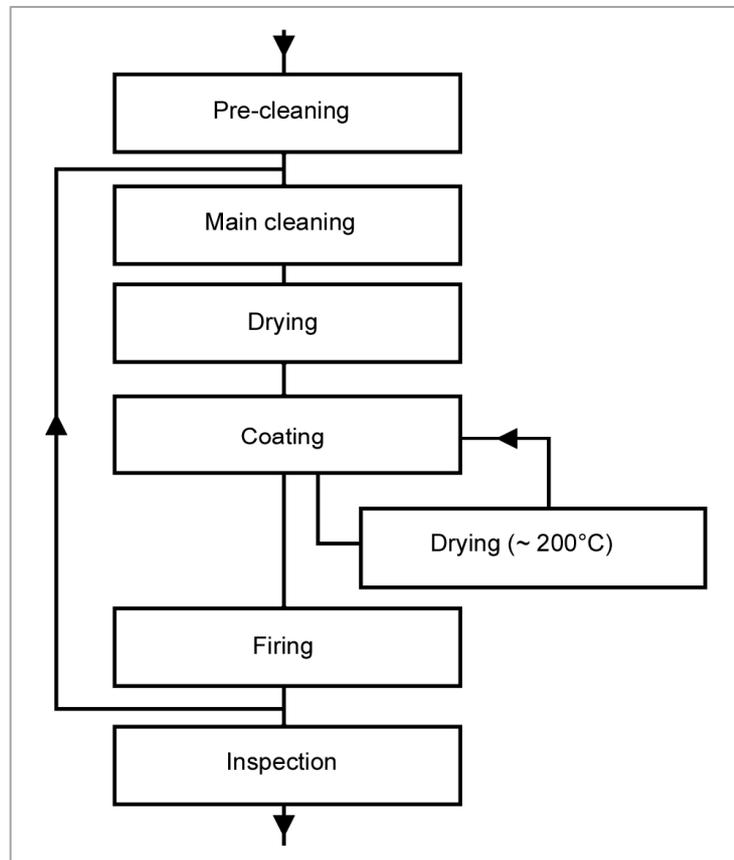


Figure 4.3.3.2.2
Production flow diagram for sol-gel coating

Figure 4.3.3.2.3 shows the flowchart of the floor plan of a sol-gel coating plant employing the dipping technique.

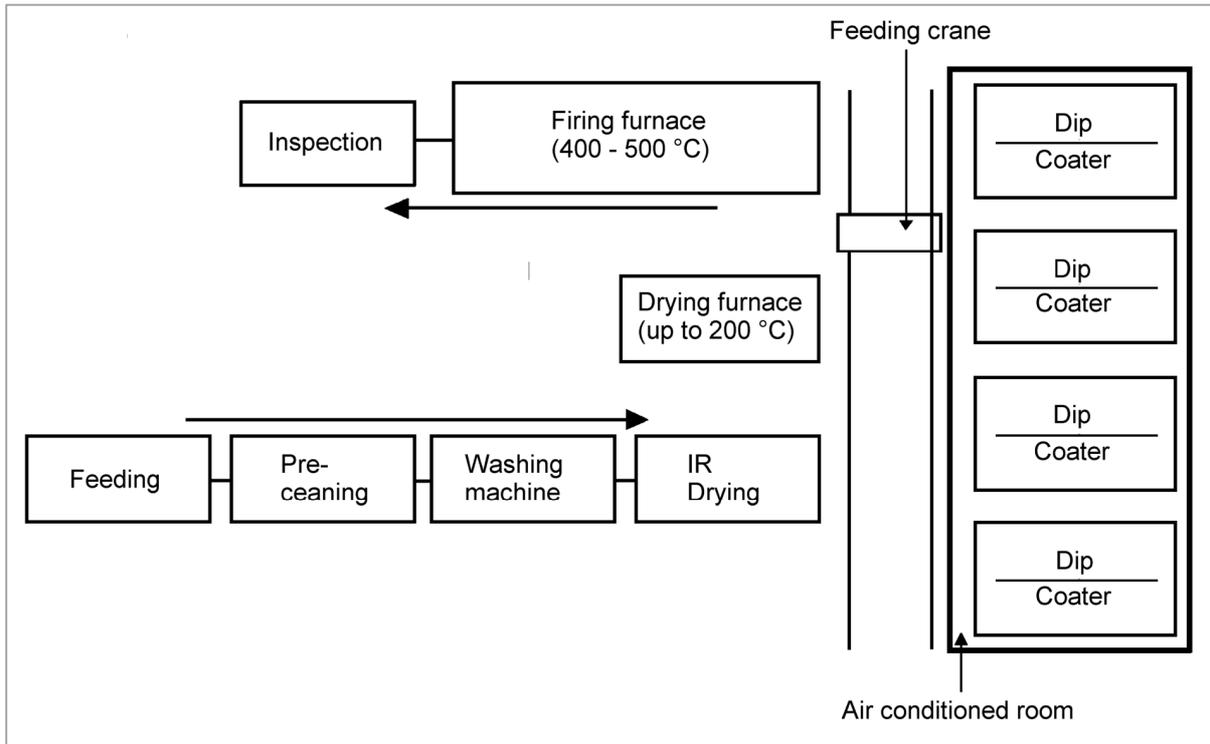


Figure 4.3.3.2.3 Flowchart of the floor plan of a sol-gel coating plant applying the dipping technique.

Mainly non-selective solar-control coatings based on TiO_2 (see Chapter 5.2, Part II), anti-reflective coating stacks of the type $\text{TiO}_2/\text{SiO}_2\text{-TiO}_2\text{-SiO}_2$ (see Chapter 5.3, Part II) and dielectric mirrors on the basis of a $\text{TiO}_2\text{-SiO}_2\text{-TiO}_2$ coating stack (see Chapter 5.4.2, Part II) are produced with this process. The maximum pane size here may be 3.21 m x 3.75 m.

The great advantage of sol-gel coating using the dipping technique is that, provided the chemical reactions can be mastered, extremely homogeneous and uniformly thick layers across the flat glass surface can be coated and thus high-quality optical coating stacks with a large number of individual layers can be produced. However, the process has the disadvantage that, despite of the relatively simple procedure, the process equipment is very costly, especially the pane cleaning stage, the air-conditioning of the room with the dip coaters and the furnace required to finally fire the layers. Moreover, even the largest plants only have a production capacity of about 50,000 m^2 per annum, i.e. sol-gel coating by dipping is suitable only for niche flat glass products manufactured in small quantities. A specific advantage is that bent panes, especially cylindrically bent panes, can also be coated. It is in the nature of the dipping technique that both sides of a pane are coated. This is advantageous for the production of anti-reflection coatings on flat glass. However, it is also possible to coat the panes on one side only with the dipping technique, by sticking two panes together before the coating process and separating them again afterwards.

It should be noted that the sol-gel coating process is increasingly used today to coat other substrates than flat glass panes.

Other sol-gel coating techniques

As mentioned above, sol-gel films can be applied using other techniques as well. It has been suggested that the coating solution could be rolled on, similar to the application of paint, or drained off over obliquely positioned panes, i.e. with the flow method. These are typical thick film application techniques which, of course, are suitable only for relatively thick layers with limited layer evenness. This might be adequate e.g. for the production of hydrophobic layers on flat glass (see Chapter 5.5.2, Part II). The chemical processes and other equipments, such as the pane cleaning stage or the firing furnace, are the same as for the dipping technique.

4.4 More recent technologies applied to flat-glass coating

Plasma-assisted CVD

'Plasma-assisted CVD' (PACVD), also called 'plasma-enhanced CVD' (PECVD), is a coating technique which has been tested and also applied industrially by several companies to coat flat glass. It is closely related to chemical vapour deposition (CVD) as described in Chapter 4.3.2.3. With both techniques, almost the same types of layers can be coated on the basis of the same coating materials. However, PACVD differs from conventional CVD in that the chemical reactions are not initiated by heat at atmospheric pressure, but by electromagnetic energy supplied by a gas discharge process, i.e. a plasma, usually under vacuum conditions. In this way, chemical and physical processes concur during a PACVD coating, for which reason this process can be classified somewhere in between physical and chemical types of coating processes. It should be noted that the energy required to form the coating can also be added in the form of light energy. This process is called light-assisted CVD (LACVD).

Figure 4.4.1 shows the basic layout of a PACVD plant.

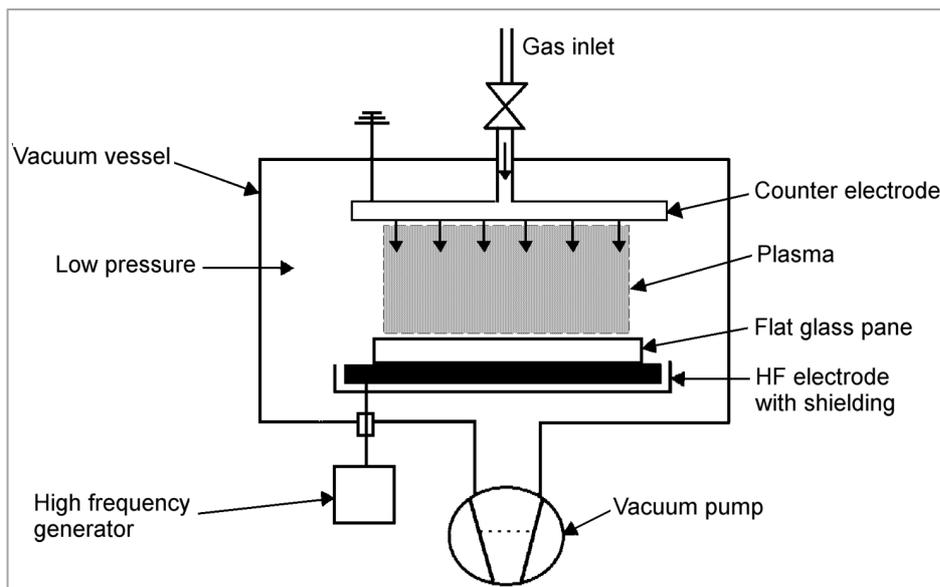


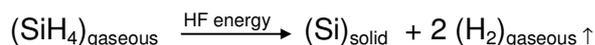
Figure 4.4.1 Schematic diagram of a PACVD plant with capacitive high-frequency coupling

The installation with capacitive high-frequency coupling is constructed similarly to that used for sputtering (see Chapter 4.2.1 and Figure 4.2.1.3.1). The basis of the coating process is the plasma of the working gas, the 'precursor', as in the conventional CVD process. However, the plasma is ignited at vacuum conditions with high-frequency (HF) electromagnetic energy. The frequency allowed for industrial processes is 13.56 MHz. Generally, the high frequency is coupled in inductively for large-area coating today. Nevertheless, the process corresponding to Figure 4.4.1 can also be run with a direct current plasma. However, using high frequency allows electrically insulating coatings or coatings on electrically insulating substrates such as flat glass.

In contrast to the sputtering process, plasma does not have the function to erode particles of the coating material from a cathode by means of ion bombardment (see Chapter 4.2.1.2), but instead decomposes the molecules of the precursor gas, splitting them up into chemical groups and/or transforming them into an electrically charged state. These decomposition products, which are chemically highly reactive, are subsequently deposited onto the substrate surface at low temperatures, under the influence of certain chemical reactions. Of course, the plasma itself also affects the coating formation during PACVD, just as in the case of sputtering processes (see Figure 4.2.1.3.2).

The main advantage of PACVD is that the plasma ensures a high decomposition rate of the coating gas and thus far higher deposition rates at lower substrate temperatures than are possible with conventional CVD. For example, the deposition rate of a silicon layer based on silane (SiH_4) as the precursor, with conventional CVD at 650°C , is only one tenth of the rate achieved using PACVD. Therefore, the use of PACVD is particularly advisable when high deposition rates with cold substrates (approximately 20°C) are to be achieved with CVD processes.

A typical chemical reaction that occurs within the PACVD process is used, for example, for the deposition of silicon layers on the basis of silane as mentioned in Chapter 4.3.2.1, according to the reaction:



or the deposition of a carbon layer on the basis of methane, according to the reaction



where the indices 'gaseous' and 'solid' describe the state of aggregation of the coating material and/ or that of the reaction products. It should be noted that the reactions are actually somewhat more complicated than is shown here. In the gas discharge zone, a number of chemical groups, e.g. CH_2 or SiH_3 , or molecules or ions are created as intermediate products, which are only reduced to carbon or silicon during further reaction steps, depending on the procedure employed. By controlling the process in a certain way, it is also possible to deposit layers which consist of or contain reaction products of the precursor which form in the plasma. If the layers are cross-linked like polymers, the process is also known as 'plasma polymerisation'. Moreover, by using additives in the precursor, the layers can be doped, resulting in quite significant alterations of layer properties (see Chapter 5.5.2.1, Part II).

Today, PACVD is used to coat flat glass with layers consisting of

- silicon (a-Si:H or c-Si:H) as absorber layers in thin-film photovoltaic cells
- porous SiO_x as anti-reflective coatings
- electrically conductive ZnO
- Si_xN_y for barrier layers and in combination with SiO_x for anti-reflective coatings
- Al_2O_3 as barrier layers.

Today, PACVD equipment is available to coat float glass panes with dimensions of up to 3.21 m x 6.00 m (“jumbo” panes).

PACVD is also industrially used to successfully coat smaller glass surfaces, e.g. to make self-cleaning spectacle lenses, chemically highly inert ampoules and bottles for the pharmaceutical industry and infrared-reflecting interference filters, a special type of dielectric mirrors (see Chapter 5.4.2, Part II) required in the manufacturing of energy-saving lamps. The deposited layers provide different functions. Spectacle lenses with a hydrophobic surface are made from modified silicon oxide, using precursors based on hexamethyl disilane (HMDS). The highly inert surfaces for pharmaceutical ampoules and bottles and the infrared reflection for energy-saving lamps are achieved with layers of oxides of silicon, titanium and tantalum or with coating stacks which consist of these oxides.

Coating with linear ion sources

Another coating technique, which some companies have tested and, in some cases, applied industrially, is the coating with linear ion sources. It is applied under vacuum conditions, i.e. it belongs to the group of PVD processes.

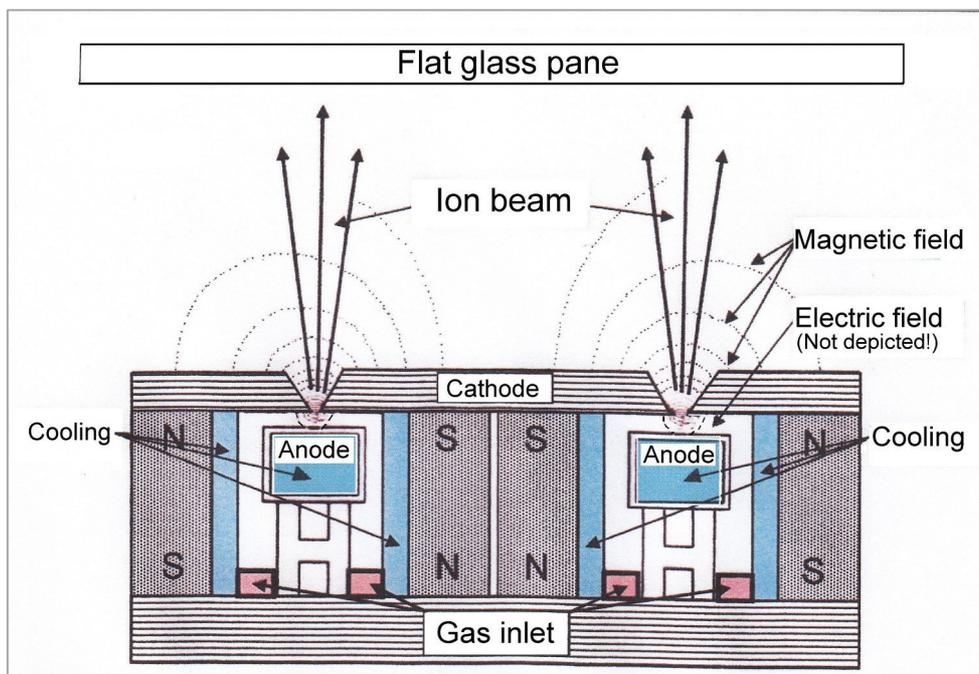


Figure 4.4.2 Diagram of a coating equipment with a linear ion source

Figure 4.4.2 shows the diagram of a coating equipment with a linear ion source. The coating technology is similar to magnetron technology; it also applies crossed electromagnetic fields to increase the ion density for the coating process (see Figure 4.2.1.5.2.2). The difference, however, is that the construction and the operating conditions are chosen such that positive

ions are accelerated toward the substrate to be coated, whereas they are accelerated toward the coating target in magnetron sputtering. Thus with ion sources, panes are coated by linear an ion beam. As the operating pressure for coating with linear ion sources is similar to that for magnetron sputtering, the two processes can be operated in parallel.

Linear ion sources are used today to deposit diamond-like carbon (DLC) coatings, which feature extremely high mechanical and chemical stability and are used e.g. to increase the mechanical and chemical resistance of the natural glass surface. In addition, linear ion sources can be used to intensively clean the substrate with a type of sputtering process immediately before the coating process, which is important particularly for the deposition of coatings that have to be tempered. Attempts have also been made to use linear ion sources to produce metal oxide or metal nitride coatings that are difficult to sputter, e.g. titanium oxide or titanium nitride more economically than by sputtering. Another tested application is to densify metal coatings e.g. thin silver layers, and thus improve their optical and electrical properties. It remains to be seen which of these approaches will be transferred to industrial application and become established there.

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