Section 3. Glass coating at atmospheric pressure

Chemical vapor deposition of coatings on glass

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Abstract

Chemical vapor deposition has been used to deposit films of a wide variety of materials. Those of particular interest to the glass industry include coatings of silicon, titanium nitride, and the oxides of silicon, aluminum, tin, zinc and transition metals, which can add very useful electrical and optical properties to glass. Several different chemical sources and reactions are used to deposit these materials. Comparison of these processes will be made in terms of ease of use of the precursors, attainable deposition rates, and safety and cost of the precursors. Equipment has been developed to deposit these materials with excellent thickness uniformity over large areas of glass. Fluorine-doped tin oxide and zinc oxide efficiently reflect infrared heat (low emissivity), thereby increasing the insulating ability of windows. These materials also conduct electricity, leading to a variety of applications, including solar cells, flat-panel displays, touch control panels, and static dissipation. Titanium nitride provides near-infrared reflectivity, which can provide high-performance rejection of solar heat (solar control glass). Silicon/silicon dioxide/silicon trilayers form durable mirror coatings with high reflectivity to visible light. Amorphous aluminum oxide films are excellent barriers to diffusion of sodium out of soda-lime glass. © 1997 Elsevier Science B.V.

1. Introduction

Numerous products are now made by chemical vapor deposition (CVD) of coatings on flat glass. These products include low-E, heat-reflecting glass, solar control glass, mirrors, anti-static coatings, abrasion-resistant coatings, sodium-diffusion barriers, and thin-film solar cells. In this paper we first review some of the materials that go into these products (Section 2), some of the CVD processes used to produce them (Section 3), examples of the equipment (Section 4) and finally the compositions and structures of some coated glass products (Section 5).

2. Materials coated on glass by CVD

Numerous materials have been produced as thin films on glass by CVD. In Tables 1–3 I list some of these materials, along with some of their optical properties. They are grouped by their electrical characteristics, according to whether they are insulating, semiconducting or metallic conductors.
Table 1
Some electrically insulating films

<table>
<thead>
<tr>
<th>Insulating films</th>
<th>Formula</th>
<th>Transmitted color</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon dioxide</td>
<td>SiO₂</td>
<td>colorless</td>
<td>1.44–1.46</td>
</tr>
<tr>
<td>Aluminum oxide</td>
<td>Al₂O₃</td>
<td>colorless</td>
<td>1.6–1.7</td>
</tr>
<tr>
<td>Silicon suboxide</td>
<td>Si₂O₅</td>
<td>colorless</td>
<td>1.5–2.0</td>
</tr>
<tr>
<td>Silicon oxydride</td>
<td>SiO₂N₂</td>
<td>colorless</td>
<td>1.5–2.0</td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>Si₃N₄</td>
<td>colorless</td>
<td>1.9–2.0</td>
</tr>
<tr>
<td>Silicon oxyacarboide</td>
<td>SiO₂C₂</td>
<td>colorless</td>
<td>1.5–2.2</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>TiO₂</td>
<td>colorless</td>
<td>2.2–2.3</td>
</tr>
<tr>
<td>Zinc sulfide</td>
<td>ZnS</td>
<td>colorless</td>
<td>2.3</td>
</tr>
<tr>
<td>Chromium(III) oxide</td>
<td>Cr₂O₃</td>
<td>brown</td>
<td>2.5</td>
</tr>
<tr>
<td>Iron(III) oxide</td>
<td>Fe₂O₃</td>
<td>brown</td>
<td>2.9</td>
</tr>
<tr>
<td>Cobalt(III) oxide</td>
<td>Co₂O₃</td>
<td>gray</td>
<td>2.9</td>
</tr>
<tr>
<td>Amorphous silicon</td>
<td>Si</td>
<td>brown</td>
<td>3–4</td>
</tr>
</tbody>
</table>

Titanium dioxide appears in both the insulating and semiconducting tables, because it may be formed in insulating or semiconducting forms, depending on the deposition conditions.

3. CVD reactions for coating glass

Numerous CVD reactions have been demonstrated to produce coatings of the materials listed in the previous section. Of course, only a few of these reactions are used regularly in production of commercial coatings on glass. In the following sections, I review some of the more commonly used reactions, and some others with potential for commercial use.

3.1. Silicon oxides

Silane is a gas that is used often as a precursor for silicon dioxide. It reacts spontaneously with oxygen even at temperatures as low as room temperature (called pyrophoric behavior). In order to slow this reaction so that a film, rather than a powder, can be formed, the concentration of silane must be kept small (<1%). Film deposition becomes faster above about 400°C. The oxidation of silane is believed to involve free radical intermediates [1]. Radical traps, such as ethylene, remove free radicals and slow down the reaction so that substrate temperatures above 600°C may be used [2]. With an excess of oxygen, this reaction produces fully oxidized films of SiO₂, with a low refractive index, around 1.45. Less oxidizing oxygen sources, such as carbon dioxide [3] or nitrous oxide [4,5] react with silane to produce silicon oxides with larger refractive indices, up to about 2.

Dichlorosilane also reacts with oxygen to produce silicon dioxide films. Particularly rapid deposition rates are found on sodium-containing substrates, such as soda-lime glass [6].

Tetraethyl orthosilicate (TEOS) is another widely used silica precursor [7–10]. Its reaction with oxygen is negligibly slow at substrate temperatures below about 700°C, so the reaction rate must be increased in order to use it to deposit silica on a glass substrate. Triethylphosphate increases the oxidation rate of TEOS, so that it can be used to coat glass rapidly.

Table 2
Some semiconducting films

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Formula</th>
<th>Transmitted color</th>
<th>Refractive index</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogenated amorphous silicon</td>
<td>Si:H</td>
<td>brown</td>
<td>3.0–3.5</td>
<td>1.1</td>
</tr>
<tr>
<td>Cadmium telluride</td>
<td>CdTe</td>
<td>red</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>Cadmium sulfide</td>
<td>CdS</td>
<td>yellow</td>
<td>2.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>TiO₂</td>
<td>colorless, blue or gray</td>
<td>2.2–2.3</td>
<td>3.0</td>
</tr>
<tr>
<td>Indium(III) oxide</td>
<td>In₂O₃</td>
<td>colorless or yellow</td>
<td>1.9–2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>ZnO</td>
<td>colorless</td>
<td>1.9–2.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Tin dioxide</td>
<td>SnO₂</td>
<td>colorless</td>
<td>1.9–2.0</td>
<td>3.5</td>
</tr>
</tbody>
</table>
at temperatures around 650°C [11]. Even lower deposition temperatures (around 400°C) can be achieved by adding ozone to the gas mixture [12,13].

Disilane derivatives are also effective silica precursors. Their reaction chemistry is initiated by cleavage of their silicon–silicon bonds [1]. By varying their substituents, substrates can be coated within a wide range of substrate temperatures. For example, methoxypentamethyldisilane [14], Me₂Si₂OMe, reacts with oxygen at temperatures of 600 to 650°C, while tetramethyldisilane [15], Me₄Si₂H₂, is effective at 500 to 600°C. Although these materials are not now commercially available, they can be synthesized readily from an inexpensive byproduct of the manufacture of silicones [16,17].

3.2. Aluminum oxide

The pyrophoric trialkylaluminum compounds (such as trimethylaluminum and triethylaluminum) are so reactive with oxygen that it is difficult to obtain a controlled CVD reaction. Nitrous oxide provides a slower oxidation reaction, but only small deposition rates are achievable [18].

Aluminum trialkoxide compounds (such as aluminum isopropoxide [19–22]) have also been used as precursors to alumina. They do not have the high sensitivity to oxygen shown by the trialkylaluminum compounds, although they do react very readily with water [23]. The main disadvantage of aluminum trialkoxide compounds is that they are difficult to vaporize reproducibly, because of their degree of polymerization varies with the age of the sample [24]. Also, most aluminum trialkoxides are solids at room temperature, making handling and metering more difficult than for liquids.

Mixed alkylaluminum alkoxide compounds (such as triethyl–dialuminum tri-sec-butoxide) combine the best features of the other alumina sources, while avoiding their difficulties. Unlike the trialkylaluminums, they are not pyrophoric. Unlike the aluminum alkoxides, they are not polymeric, and are low-viscosity liquids that are easier to handle and to evaporate reproducibly. They are readily synthesized from inexpensive raw materials. For example, triethyl–dialuminum tri-sec-butoxide can be made by mixing and heating triethylaluminum and aluminum sec-butoxide, both of which are inexpensive materi-

als produced commercially in large quantities. Glass temperatures around 600°C cause rapid deposition of smooth, amorphous and transparent layers of aluminum oxide from alkylaluminum alkoxide compounds. By adding oxygen to the gas mixture, lower glass temperatures, around 400°C, can be used to deposit aluminum oxide without distorting the flatness of cut glass substrates.

3.3. Titanium dioxide

The most common CVD source for titanium dioxide is titanium isopropoxide [25,26]. This liquid is the most volatile of the titanium alkoxides. It reacts at temperatures around 450°C to form polycrystalline titanium dioxide (usually the anatase form) without any added oxygen source, using some of the oxygen contained within the source molecules. Adding some molecular oxygen gas to the deposition atmosphere allows reaction to take place at lower temperatures. Mixing water vapor in the vicinity of the glass surface decreases the deposition temperature further, to 250°C or less, and deposit is amorphous with a smaller refractive index. Films deposited under all of these conditions are electrical insulators.

Electrically conductive titanium dioxide films can be deposited from vapor mixtures containing titanium isopropoxide and a few per cent niobium or tantalum ethoxide at temperatures around 450°C [27]. Addition of cyclohexane vapor reduces the resistance further [28].

3.4. Other transition metal oxides

The oxides of cobalt, iron and chromium are most commonly deposited from the acetylacetonates of these metals. These compounds (from the chemical class called beta-diketonates) are solids which can be sublimed into the vapor phase and then carried by a carrier gas into a CVD apparatus.

These same acetylacetonates have also been used in a spray pyrolytic method, in which spray nozzles project droplets of a solution of these materials at a hot glass surface [29]. The most commonly used solvents for these materials are chlorinated organic solvents, such as methylene chloride. Normally both the organic solvent and the solute metal acetylacetonate vaporize before reaching the glass surface. Disposing of the resulting large amount of organic
solvent vapor has made this solution method less popular. In an alternative pyrolytic method which avoids the use of any solvent, a fine powder of the solid is suspended in a carrier gas (usually air) and blown at the hot glass surface, where the powder sublimes into a vapor and reacts immediately to form the oxide coating. The powder may also be suspended in water (in which it is nearly insoluble), and the suspension sprayed onto the glass [30]. All these spray and powder methods are essentially variant CVD processes, which distribute the same vapor over a hot glass surface by different means.

3.5. Silicon

Silicon films are normally deposited on hot glass surfaces by CVD from silane gas, SiH4. The deposition rate becomes sufficiently rapid for on-line glass coating at glass temperatures around 650°C. The silicon deposited under these conditions is normally amorphous, rather than crystalline. Polycrystalline silicon can be deposited at higher temperatures, but special glasses with high softening points must be used as substrates. Lower deposition temperatures, 400 to 500°C, can be used with disilane, Si2H6, as a precursor. This amorphous deposit contains appreciable amounts of hydrogen, up to 10 at.% [31].

3.6. Zinc oxide

Diethylzinc is the most common precursor for zinc oxide. Its reaction with water vapor occurs rapidly at substrate temperatures as low as 200°C. Alcoholics act as oxygen sources at higher substrate temperatures: tert-butanol at about 300°C, isopropanol at 400°C, and ethanol at 450°C. Liquid diethylzinc is pyrophoric, so it requires careful handling to avoid fires. Its reaction with oxygen produces powder even at low concentrations of oxygen, so oxygen must be rigorously excluded from the deposition region. A safer version of diethylzinc is obtained by reacting it with a tertiary amine chelating agent, such as tetramethylethylenediamine. The product of this reaction is not pyrophoric, but still enters into the CVD reactions producing zinc oxide.

3.7. Tin oxide

Tin oxide has been deposited from a very wide range of tin compounds, with ligands including alkyl groups, halogens, carboxylates and alkoxides. Tin tetrachloride is a popular and inexpensive tin source, which is usually reacted with water vapor as an oxygen source [32,33]:

\[
\text{SnCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SnO}_2 + 4\text{HCl}. 
\]

This reaction is very fast, so moderators such as alcohol [34] or hydrogen [35,36] are often added. Attaching alkyl groups in place of some of the chlorines also moderates the reaction with water vapor, making it easier to control. Butyltin trichloride [37] and dimethyltin dichloride [38] are examples of suitable alkyltin chlorides.

3.8. Metals

Aluminum may be deposited from aluminum alkyls, such as di-isobutylaluminum hydride, and from amine complexes of aluminum hydride. Initiation of the growth reaction is erratic on glass surfaces, however. Tungsten is normally grown by reduction of tungsten hexafluoride by hydrogen, but adhesion of tungsten films to glass surfaces is weak [39]. For these reasons, CVD of these metals on glass has not been practiced commercially.

3.9. Titanium nitride

Titanium nitride can be formed on glass substrates by reaction of titanium tetrachloride and ammonia [40,41]:

\[
6\text{TiCl}_4 + 8\text{NH}_3 \rightarrow 6\text{TiN} + 24\text{HCl} + \text{N}_2. 
\]

These vapors may be mixed prior to entering a CVD apparatus, provided they are heated to a temperature of about 250°C to 320°C before mixing. Titanium nitride deposition from this homogeneous mixture occurs uniformly on substrates heated to temperatures above 500°C.

3.10. Titanium silicide

Deposition of titanium silicide can be carried out by reaction of titanium tetrachloride vapor and silane [42]:

\[
\text{TiCl}_4 + 2\text{SiH}_4 \rightarrow \text{TiSi}_2 + 4\text{HCl} + 2\text{H}_2. 
\]

Substrate temperatures of 600 to 650°C are suitable for this reaction.
4. Equipment for production of CVD coatings on glass

The essential functions of CVD equipment are to create an appropriate vapor or gas mixture, and to make it flow over a glass surface heated to an appropriate temperature. In most applications to making large areas of coating, CVD processes are carried out at normal atmospheric pressure. In some specialized applications, particularly in the semiconductor industry, CVD is often carried out at lower pressures. In this review, we will concentrate attention on apparatus used for making large-area coatings at atmospheric pressure.

If the reactants are gases, then an appropriate gas mixture can be formed using standard gas flow controllers. If a reactant is a liquid or solid, it must first be vaporized. Often the vaporization is done in a ‘bubbler’, by passing a carrier gas through a precursor, which is heated if necessary to increase its vapor pressure. Vaporization of liquids or solutions may also be accomplished with a stirred thin-film evaporator (Fig. 1) [43].

In most products, a coating with uniform thickness is desired. If CVD is carried out on a stationary substrate at atmospheric pressure, the thickness of coating varies with position along the surface. Usually there is a maximum thickness along the direction of gas flow, as indicated in Fig. 2, which shows

![Fig. 2. Silicon dioxide growth rate as a function of distance from the gas inlet, for the CVD reaction of disilane, Si$_2$H$_6$, (0.2 mol%) and nitrous oxide, N$_2$O, (80 mol%), for three substrate temperatures. The points are experimental and the lines are theoretical, from [3].](image)

![Fig. 1. Schematic cross-section of a thin-film evaporator. The liquid flow is metered through tube 17 into a heated cylindrical cavity 13, into which a metered flow of carrier gas enters through tube 18. Wiper bars 24 spread the liquid over the heated cylindrical surface so that it may evaporate quickly into the carrier gas [43].](image)

![Fig. 3. Schematic diagram of an on-line CVD coater producing turbulent gas flow through nozzles 43, including a spray vaporization chamber 12 [37].](image)
the thickness distribution of a CVD silicon dioxide film. The coating is thinner at the beginning of the gas flow, where the gas first reaches the surface, because chemical reactions in the gas convert the reactants into more reactive chemical intermediates as the gas flows along the hot surface. As the concentrations of these reactive intermediates grow, the deposition rate increases, eventually reaching a maximum. After that, the concentrations of the reactive intermediates decrease, as the original reactants are consumed and used up. By the time the gas reaches the exhaust, most of the reactants have been depleted.

In order to produce a uniformly thick coating, the glass substrate is moved in the same direction as the gas flow, so that each part of the surface is exposed to the entire profile of non-uniform coating rates. If the gas is also distributed uniformly across glass width (in the direction perpendicular to the motion of the gas and the glass), then a uniformly thick coating will result. In order to achieve this result, not only must the reactant gas mixture be injected at a uniform flow rate across the width of the glass, but also the depleted gas must be uniformly removed by an exhaust slot or slots going across the width of the glass.

A variety of special pieces of equipment have been developed in order to make coatings with uniform thickness over large areas. It is usual to distinguish between CVD processes operated on a continuous glass ribbon in a float glass production line ('on-line coating'), and processes run on cut pieces of reheated flat glass in a belt furnace or roller furnace ('off-line coating'). The desired conditions of uniform gas distribution and uniform coating thickness can be approached more closely in continuous 'on-line' production than in 'off-line' processes, which are subject to transient disruptions as each piece enters or leaves the coating region. Despite this difficulty, belt furnaces are widely used for CVD of coatings in the semiconductor and solar cell industries. Commercial 'off-line' CVD equipment is made in the USA by the Watkins-Johnson Company (Scotts Valley, CA), BTU International (North Billerica, MA) and Sierratherm (Watsonville, CA). Systems with belt widths up to about 0.6 m width have been produced.

Equipment for 'on-line' CVD coating has been developed by several primary flat-glass manufacturers, producing uniform coatings over 3 m wide. One of the earliest on-line coaters was designed at PPG Industries for CVD of transition metal oxides; a schematic diagram of this apparatus is shown in Fig. 3. This system evaporates a liquid solution of the metal compounds by spraying the solution into an upper chamber, and directs the vapor mixture down-

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Fig. 4. Schematic cross section of an on-line CVD coater with uni-directional laminar gas flow from the gas distributor 33 along the gas flow path 47 to the exhaust slot 44 [64].
ward at the glass surface under turbulent flow conditions (high Reynolds number gas flow). Pilkington designed an on-line coater for silicon deposition from gaseous silane; a schematic cross-section of their design is shown in Fig. 4. In this equipment, the reactant gas flows more slowly, in a laminar manner (at a low Reynolds number) in the same direction as the glass moves, into a single exhaust slot. Use of two exhaust slots, one upstream (number 30 in Fig. 5) and the other downstream (number 34 in Fig. 5), provides more complete isolation of the bi-directional laminar reactant gas flow (coming out of slots number 26 and 28 in Fig. 5) from the ambient atmosphere (numbers 12 and 20 in Fig. 5). Another bi-directional laminar-flow coater is shown schematically in Fig. 6. If two CVD precursors are so reactive that they cannot be mixed together before they reach the glass surface, then the two vapors can be separately introduced, by apparatus such as shown in Fig. 7.

CVD reactants have also been delivered as liquid spray droplets. A typical on-line spray system is sketched in Fig. 8. The three spray heads are moved quickly back and forth across the glass ribbon, in order to form a coating with uniform thickness. The
solution droplets are made small enough so that they evaporate as they approach the hot glass surface. Systems for distributing powdered solid reactants across a moving float glass ribbon have also been developed (Fig. 9). The jet mill breaks up the powder into extremely fine dust with particles a few
microns in diameter. When the dust comes close to the surface of the hot glass, it sublimes into a vapor that reacts to deposit a uniform film on the hot surface.

5. Products based on CVD coatings on glass

Functional coatings for various applications are formed by CVD of one or more layers of the materials listed in the tables. The simplest products are of course single-layer coatings, but most products require two or more coatings of different materials to achieve all the desired properties.

5.1. Sodium-diffusion barriers

The sodium in soda-lime glass can diffuse from its surface and cause degradation of structures deposited on its surface. For example, tin oxide deposited on soda-lime glass has higher electrical resistance than when it is deposited on alkali-free substrates. Liquid crystal displays also need to be protected from sodium. This protection can be accomplished by using low-sodium glass substrates, but a less expensive solution is to deposit on soda-lime glass a thin film which acts as a diffusion barrier. Silicon dioxide is most commonly used for this purpose. Even thin layers of CVD silica, a few tens of nanometers thick, can substantially reduce the diffusion of sodium from a soda-lime glass surface [44,45].

Silica, however, does not completely stop the diffusion of sodium, particularly at elevated temperatures, because the rather open tetrahedrally-bonded structure of silica [46] provides sufficient open space through which the sodium can diffuse. Various tests may be applied to measure the sodium permeability of a silica layer. We did this by depositing a layer of CVD tin oxide over the silica, and then dissolving the tin oxide layer and measuring the sodium content of the etchant solution [47].

Similar tests on CVD amorphous aluminum oxide layers showed that alumina is a more complete barrier to diffusion of sodium. In fact, to within the sensitivity of our test method, we could not detect any diffusion of sodium through the alumina films [48]. Aluminum oxide has a more closely-packed solid structure [49], which may account for its better performance as a barrier.

5.2. Low-E glass

Energy-conserving window coatings reflect the heat carried by infrared radiation with long-wavelengths, around 10 μm. This effect is achieved by CVD coatings incorporating fluorine-doped tin oxide as the active layer. The fluorine is added at small concentrations (around one at%) to produce conduction-band electrons in the semiconductor tin oxide. These free electrons reflect the infrared radiation, almost doubling the insulating property of a window. A tin oxide film only 1/3 of a μm thick can reflect over 85% of the heat, and the reflectivity of thicker films can be as high as 90% [50].

Tin oxide films of sub-micron thickness are transparent, but show strong iridescent colors that look like an oil slick on the glass. These iridescent colors can be hidden by depositing one or more suitable transparent layers between the glass and the tin oxide [51]. For example, an intermediate layer 70 nm thick of refractive index about 1.7 suppresses the iridescent colors. CVD coatings of mixed silica–tin oxide can have their composition adjusted to have the correct refractive index [52]. CVD silicon–carbon–oxygen mixtures [53], silicon–nitrogen–oxygen mixtures, or alumina–titania mixtures can be tuned similarly to a refractive index of 1.7. Another color-suppression method, which does not require adjustments to the refractive index, is to apply first a 25 nm layer of tin oxide, then a 25 nm layer of silica, and finally the fluorine-doped tin oxide [54]. The challenge of depositing layers with these properties and sufficient uniformity has been met by glass manufacturers in the production of their hard-coated low-E glazing products.

5.3. Electrical applications of fluorine-doped tin oxide

The conduction electrons in fluorine-doped tin oxide provide it with low electrical resistance, which can be as small as 8 ohms per square at a thickness of about 0.4 μm. This transparent conductor on glass has now been incorporated into many products. Freezer display cases are heated to prevent frost
from obscuring them. Anti-static coatings are placed on Xerographic copier windows. Touch controls on a variety of appliances are made from tin oxide-coated glass. Electrodes for flat-panel displays can be etched from tin oxide films. Thin-film solar cells are constructed on tin oxide-coated glass, by adding layers of semiconductors, such as amorphous silicon [55] or cadmium telluride.

Tin oxide coatings on glass are more abrasion-resistant than the glass itself. This property has found use in protecting glass in areas such as laser scanner windows at supermarket check-out counters.

5.4. Solar control glazings

Many types of solar control glazing have been developed to limit the ingress of heat and light, to avoid excessive solar heat and visible glare in large buildings. Body tints are introduced into the glass itself, by various additives, such as iron oxide, nickel oxide, cobalt oxide, chromium and selenium [56]. A disadvantage of body tints is that it takes the manufacturers a long time to change over production from one color to another, resulting in lost production.

Solar control may also be achieved by various coatings deposited on glass. CVD production of these coatings can be started and stopped much more quickly than body tints. Coatings containing the mixed oxides of cobalt, iron and chromium absorb visible light and infrared heat [57]. Adjusting the composition of these coatings provides a range of muted colors, or a neutral gray coating.

Care is required in the design and use of absorbing tints or coatings in large windows, because the absorbed solar heat can cause breakage. Silicon coatings reflect more light and heat, and absorb less than the metal oxides [58]. Thus the possibility of breakage by thermal stress is reduced. The durability of silicon coatings is increased by adding a protective layer of tin oxide [59].

Solar control coatings of titanium nitride give even better performance, because they reflect, rather than absorb, near infrared radiation in sunlight [60]. Thus, the near-infrared solar heat is excluded more completely. Titanium nitride also reflects longer-wavelength radiation. This low-emissivity property means that a window's insulating ability is also increased by a titanium nitride coating. An overcoat of tin oxide protects titanium nitride from oxidation during tempering, and from abrasion during use [61].

Titanium silicide can also be used as a solar control film. It has the advantage of having a neutral color in both reflection and transmission. It also must be protected from oxidation and abrasion [62].

5.5. Mirror coatings

Most mirrors are made by evaporating aluminum or depositing silver from aqueous solution. These metal mirrors are subject to corrosion, oxidation and tarnishing. More durable mirrors may be made by CVD of alternating thin layers of silicon and silicon dioxide [63].

6. Conclusions

Chemical vapor deposition has been established as an effective method for depositing uniformly thick, high-quality coatings of certain materials on large areas of flat glass. Suitable chemical precursors have been identified for many oxides, nitrides, silicides, silicon and metals. Large-scale equipment has been developed for making CVD coatings either during float glass production or on cut pieces of glass. Atmospheric pressure CVD is a cost-effective process, in comparison with other methods for depositing thin films, such as sputtering, vacuum evaporation, glow discharge, sol-gel dipping and electroless deposition.

References

[58] Kirkbride et al., Belgian patent 830,179.