Short Communication

High transmission float glass for solar applications[1)]

Walther Glaubitt, Dieter Sporn and Eckart Hußmann
Fraunhofer-Institut für Silicatforschung, Würzburg (Germany)

Andreas Gombert and Volker Wittwer
Fraunhofer-Institut für Solare Energiesysteme, Freiburg (Germany)

Antireflective quarter-wave single layers with an improved abrasion resistance were prepared from sols by dip coating of float glasses, which can be used for covering solar cells and collectors. The coating sols are based on tetraalkoxysilane hydrolyzed in the presence of different organic additives, eg. polymers. This kind of sols lead to a stable pore structure in the pre-annealed film, which allows to treat it even at temperatures neccessary for glass strengthening. A heat treatment above 600 °C improved the abrasion resistance, but was not accompained by a reduction of the pore volume as would commonly be expected. The resulting porous film therefore showed the required effective refractive index of < 1.3, and increased the transmission of such coated low-iron glass up to 99.6 % in the visible spectral range and 97.0 % in the solar spectral range.

Hochtransmissives Floatglas für solare Anwendungen

Antireflektierende λ/4-Schichten mit einer verbesserten Abriebbeständigkeit sind auf Glasscheiben, die für Solarkollektoren bzw. Photovoltaik-Module verwendet werden können, durch Tauchbeschichtung aufgebracht worden. Die hierfür verwendeten Beschichtungssole wurden aus Tetraalkoxysilan hergestellt, das in Gegenwart verschiedener organischer Zusätze, beispielsweise Polymere, hydrolysiert worden ist. Schichten aus diesen Solen weisen eine stabile Porenstruktur auf, die Temperaturen, wie sie zum Vorspannen von Glas nötig sind, widersteht. Eine Temperaturbehandlung oberhalb 600 °C verbessert die Abriebbeständigkeit der Schicht, ohne daß dabei das Porenvolumen verkleinert wird. Die resultierenden porösen Schichten weisen daher die erforderliche Brechzahl < 1.3 auf und erhöhen die Durchlässigkeit von so beschichtetem Glas mit niedrigem Eisengehalt auf bis zu 99.6 % im sichtbaren und 97.0 % im solaren Spektralbereich.

1. Introduction

When sun light passes across the boundary of air to glass, part of the energy is reflected, e.g. 4 % in the case of visible radiation at normal incidence. The losses by reflection of glass panes which are used for covering solar systems, as for example photovoltaic cells or solar thermal collectors, reduce their efficiency.

Various concepts exist to suppress reflection on glass. However, most of them are dense multilayers which successfully reduce reflection only within a narrow spectral band, e.g. the visible range. A single layer on glass can lead to a very good antireflective effect at the glass-air boundary with a wider bandwidth than that of interference multilayers if its refractive index is equal to the square root of the refractive index of the glass substrate. For a homogeneous quarter-wave layer on glass (n = 1.5), the ideal refractive index is 1.22 according to Fresnel's formula, a principle that has been known for more than 150 years. Layers having such a low refractive index can be achieved by mixing a solid material with air on a subwavelength scale to reach a porosity of about 50 %. When the structural dimensions are smaller than the wavelength of light, the structures cannot be resolved, and the porous layer acts as a homogeneous medium, in which the effective refractive index is determined by the fractional volume of the solid material.

Methods for the preparation of such layers on glass have already been known since 1943. They can be divided into three approaches, first, etching of the glass substrate itself, second, depositing a porous coating on the glass surface and, third, a combination of both. In

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the latter case, coatings with a still too low porosity are subsequently etched. Porous surfaces produced by etching of the substrate material lead to very good optical results as well as to good durability of the surfaces [1]. The substrate material, however, is limited to phase-separated glasses, eg. borosilicate glasses with suitable compositions [2]. The large volumes of acids used (e.g. NH_4F-HF and $H_2SiF_6 \cdot SiF_4$), are the major disadvantage of this technology which causes environmental concern.

A good compromise between optical and mechanical properties is given by porous sol-gel single layers, which can be produced in a dip- or spin-coating process. Many years ago, in 1943 Moulton [3] used tetraalkoxysilane, ethyl acetate, ethanol, water and HCl for preparing sols, which were aged for several days before application. The dispersed particles obtained by aging the sol produced a porous coating which enhanced the transmission up to 98 % on glass with a refractive index of 1.52. In 1983 Yoldas [4] improved the transmission of quartz substrates up to 99.5 % throughout the range of 300 to 1100 nm by etching Moulton's porous layers after they had been annealed at up to 600 °C, and he pointed out that silica tends to sinter at temperatures higher than 400 °C. The densification caused a loss of porosity and therefore a rise in the coating reflectance with a refractive index higher than 1.22 [5]. A desirable level of abrasion resistance, however, was achieved only in that high-temperature range, at the softening point of the glass [6] or at least at 550 °C [7]. Due to the densification behavior of these silica films efforts were directed towards a better abrasion resistance and maintaining maximum optical properties at lower temperatures. Thomas [8] investigated a mixture essentially developed by Moulton [6] that consisted of silica particles in a soluble siloxane matrix, but he had to conclude that polysiloxane acted both as a binder and a filler, hence an improvement of the abrasion resistance in any case was combined with an increasing refractive index. Floch [9 and 10] improved the abrasion resistance by replacing the siloxane binder with a polytetrafluoroethylene-derived organic polymer, but he could not avoid the rise of the refractive index of such films either. Therefore, one could conclude that etching of films treated at high temperature is necessary in order to produce abrasion-resistant porous silica containing films with perfect optical performance on common glass substrates.

Figure 1. Highly transmissive glass pane for solar applications.

2. Newly developed porous silica layers

In a cooperation of two Fraunhofer Institutes we have developed a process which can be utilized on an industrial scale and allows cost-efficient production of highly transmissive float glass for solar applications [11]. Glass panes with a size adjusted to thermal solar collectors or photovoltaic cells are dip-coated in newly developed silica comprising solutions and afterwards hardened at temperatures > 600 °C (figure 1).

The withdrawal rate determines the thickness of the remaining wet film and influences its homogeneity. Both thickness and homogeneity depend furthermore on the humidity, the temperature and the convection of air while the wet film is drying. Further parameters which had to be optimized were the glass surface, the wet film deposited on it, its viscosity and the volatile components within the film. Thus, a thickness deviation of the porous layers of less than 5 nm was achieved within a range of 100 to 150 nm. The newly developed coating solutions contain organic additives such as polymers and functionalized alcohols, which affect the hydrolysis and condensation process of the tetraalkoxysilane used. Additionally, the morphology of the resulting inorganic skeleton is modified in such a way, that after strenghening of the glass an inorganic layer with improved abrasion resistance and excellent optical properties is formed.

Figure 2 illustrates the behavior of corresponding wet films deposited on polished quartz substrate after exposing it directly to different temperatures up to 1200 °C. Each sample was kept for 15 min at the temperature mentioned.

The reflection values measured after thermal treatment show an almost constant low level up to 1000 °C. A steep increase due to the densification of the pores occurs above this temperature. At lower temperatures only a slight variation of reflectance is observable. We assume that the sintering of skeleton improved its mechanical stability and therefore the abrasion resistance of the layer.

Comparable results were achieved on glass with a low iron content. Such glass having a solar absorption of 1 % was coated and subsequently hardened at 630 °C. It showed a solar transmission of > 96.5 % and 99.6 %

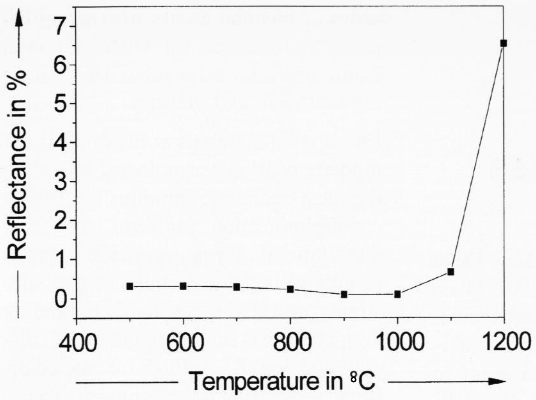

Figure 2. Films from organically modified silica sols deposited by dip-coating on quartz substrates and treated subsequently for 15 min at different temperatures as indicated in the graph.

in the visual range. The layer itself revealed no refraction gradient according to ellipsometric measurements. That means that the optical values of the layer are very close to the theoretical limit.

In tests lasting more than two years, the coated glasses proved very efficient. They are cleaned by rain from adhering dust so that their high transmission is always restored. After 26 months, no degradation of the layers could be found. In addition, the new porous layers passed climate tests in presence of noxious gases like SO_x. Abrasion tests commonly used for optical layers were also fulfilled.

3. Conclusion

A process which allows the production of porous SiO_2 layers with an improved abrasion resistance on glass was developed. The porous layers showed the required refractive index of < 1.3, and increased the solar transmission of low-absorption glass up to 97 %. The coated glasses are durable and are kept always clean by rainfall in outdoor applications. Therefore, they are highly suitable for applications like covering of photovoltaic cells or solar thermal collectors. The newly developed process is now being transferred to production scale together with partners from industry.

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Addresses of the authors:

W. Glaubitt, D. Sporn, E. Hußmann
Fraunhofer-Institut für Silicatforschung
Neunerplatz 2
D-97082 Würzburg

A. Gombert, V. Wittwer
Fraunhofer-Institut für Solare Energiesysteme
Oltmannsstraße 5
D-79100 Freiburg