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Compatibility of antireflective coatings on glass for solar applications with photocatalytic properties

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Abstract

Antireflective coatings for solar cover glasses and photocatalytic coatings for self-cleaning glasses are two types of nano-functionalized thin films, which are extensively investigated at present. Broadband antireflective coatings typically receive their function by the low refractive index of nano-porous silica (<1.4), whereas the most established photocatalytic coatings consist of high refractive index materials, such as titania (>2.0). Compatibility of these two functional materials was investigated using sol–gel dipcoating-technology. Therefore silica sol, used to prepare nano-porous antireflective coatings, was mixed with different amounts of titanium n-butoxide to achieve titania concentrations in the range from 1 to 50 wt%. The fired coatings on silica glass showed a decrease in solar transmittance and an increase in photocatalytic activity with increasing titania concentration. With respect to applications in solar energy conversion systems compatible SiO_2–TiO_2 materials of low titania fractions (10 wt%) were established, which combine minor loss in transmittance and exceptional high photocatalytic activity. In comparison to conventional nano-porous silica, the decrease in the solar transmittance was only 0.7%, whereas the degradation rate of stearic acid was 30 times faster.

Keywords: Sol–gel; Antireflection coating; Self cleaning; Solar cover glass; Bifunctional; Photocatalytic activity

1. Introduction

The efficiency of solar power plants for the production of electricity as well as solar collectors for heating water depends primarily on the intensity of the incident sunlight. Also for greenhouses a high transmittance for the visible light, where photosynthesis is initiated, is desirable (Silverstein, 1980). A basic drawback of any transparent cover material used to minimize convection and radiation losses is the reflection of the incident sunlight at its surfaces.

Therefore, porous silica layers are widely used as antireflection (AR) coatings for solar collector covers (Cathro et al., 1984; Gombert et al., 2000; Helsch et al., 2000; Kesmez et al., 2010; Nostell et al., 1999; Thomas, 1992; Troitskii et al., 2009; Wu et al., 2000). Quarter wavelength coatings with an optimized film thickness of 110 nm and a porosity of about 35% increase the light transmission of borosilicate glass at 550 nm from 92% to 97% (Helsch et al., 2006). In the same way the solar transmittance of silica glass is increased from 93% to 97% (Deubener et al., 2009; Helsch et al., 2010).

During outdoor service AR coatings are exposed to various environmental influences, such as sand storms, hail, native salt atmospheres, dust particles as well as airborne volatile organic compounds. All these factors will lead to a decrease in solar transmittance if they damage or contaminate the AR coating. Thus, Cathro et al. (1981) described that adsorbed airborne contaminants decreased transmission during exposure tests considerably. The decrease was

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attributed to filled pores of the thin film, which led to an increase in the refractive index and hence to a higher reflectance. Also Pareek et al. (2008) determined an increase in refractive index of porous antireflective coatings due to oil vapor contamination.

Enhanced chemical durability and self cleaning ability were addressed to tackle the problem of contamination induced reflectance of porous AR coatings (Thomas et al., 1999; Pareek et al., 2008; San Vicente et al., 2010). San Vicente et al. (2010) decreased the surface reactivity by exchanging active silanol groups to inert organosilyl groups. The treated surfaces remained cleaner for longer times and high solar transmittance was prolonged.

A further possibility for conserving high solar transmittance is the combination of a porous antireflective coating with a photocatalytic active material since solar UV-radiation can induce catalytic processes on synthetic and natural surfaces (Parmon and Zakharenko, 2001). The photocatalytic effect of semiconductor metal oxides especially TiO_2 has received much attention in recent years for purification and treatment of polluted water and air (Negishi and Takeuchi, 2001; Sakthivel et al., 2006; Deubener et al., 2009) as well as for self-cleaning surface applications (Watanabe et al., 1999). The self cleaning effect was based on both photo-oxidation of organic compounds to water and carbondioxide (Mills and Lee, 2002) and photoinduced superhydrophilicity (Watanabe et al., 1999). Titania in the anatase form is the most investigated photocatalyst offering excellent photocatalytic activity (Fretwell and Douglas, 2001; Moiseev et al., 2011; Qi et al., 2011; Yeung et al., 2003).

Recently, combinations of antireflective with photocatalytic properties have been achieved by preparing SiO_2/TiO_2-double-layers. The photocatalytic activity of these bifunctional coatings was quantified by measuring the degradation of organic films deposited on the surface of the double layer using IR-spectroscopy (Zhang et al., 2006), contact angle measurement (Liu et al., 2008; Zhang et al., 2005) and ellipsometry (Faustini et al., 2010). Other authors used the degradation of rhodamin B (Burunkaya et al., 2010; Kesmez et al., 2009) or methylene blue (Prado et al., 2010) in aqueous solutions. A common result of these studies was the decrease of the antireflective properties and an increase of the photocatalytic activity with increasing titania layer thickness. Further, double-layer systems were bound to time and energy intensive preparation of two subsequent coating steps.

In this paper a bifunctional SiO_2/TiO_2-single-layer is prepared in one coating step by mixing silica and titania precursors in a single coating solution. This procedure will comprise the mismatch in refractive indices of the two materials since on one hand the very low refractive index of nano-porous SiO_2 ($n < 1.4$), is prerequisite for the broadband AR function and on the other hand high refractive TiO_2 ($n > 2.0$) is needed for effective photocatalysis. Compatibility of these apparently conflicting optical properties in terms of solar transmittance and photocatalytic degradation of stearic acid is presented.

2. Experimental

2.1. Preparation of sol–gel thin films

Two different precursor solutions were prepared using silica sol (Köstrosol 2040, Bad Köstritz, Germany) diluted with 2-propanol under acid conditions and titanium n-butoxide (Fluka, Germany) diluted with 2-propanol and stabilized with ethyl acetoacetate. Both precursor solutions were mixed together in different amounts to obtain coating compositions of $x\mathrm{TiO_2} \cdot (100 - x)\mathrm{SiO_2}$ with titania concentrations $x = 1.0, 2.5, 5.0, 7.5, 10, 20, 30, 40$ and 50 (wt%). Also pure silica and pure titania coatings were prepared for comparison. Silica glass slides of 1 mm thickness were coated by dip-coating technology with a coating speed of 1 mm s^{-1} to achieve a film thickness of 110 nm for pure silica layers. The dip-coated glasses were heated in air at 20 K min^{-1} up to 550 °C using an electrical resistance furnace, held at 550 °C for 30 min and cooled down in the closed furnace to room temperature. Dwelling at 550 °C for 30 min yield to crystallization of anatase (Liu et al., 2007; Yu et al., 2000) while transformation to rutile was not observed.

2.2. Film thickness and adhesion

For measuring the coating thickness, the freshly prepared, unfired coating was scratched with a plastic knife without damaging the substrate. After heat treatment the depth of the scratches was measured by profilometry using a Tencor P-1 Long Scan Profiler, Texas Instruments. Adhesion of the fired coatings was tested manually by wiping with a paper tissue.

2.3. Nanostructure

Film structure was investigated by a Helios NanoLab 600 (FEI™, Eindhoven, Netherlands) field emission scanning electron microscope (FESEM) equipped with a focused ion beam (FIB). This dual beam FIB/SEM system enables the precise preparation and imaging of defined cross sections. The intensities of the backscattered electrons were used to image chemical composition of the cross sections, whereas the secondary electron mode was used to get high contrasted top views.

2.4. Solar transmittance

Solar transmittance τ was measured using a Perkin Elmer Lambda 950 UV/VIS-IR spectrometer equipped with an integrating sphere (150 mm) according to standard procedure (DIN EN 410). In this norm the average transmittance τ in the wavelength range from $\lambda = 300$ to 2500 nm is weighted by the air mass 1.5 radiation and calculated as

$$\tau = \frac{\int_{300\ \mathrm{nm}}^{2500\ \mathrm{nm}} T_\lambda \cdot S_\lambda \cdot d\lambda}{\int_{300\ \mathrm{nm}}^{2500\ \mathrm{nm}} S_\lambda \cdot d\lambda} \quad (1)$$