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Large area, low cost anti-reflective coating for solar glasses

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ABSTRACT

We present *on line* formation of a sol from wet-deposited aqueous potassium silicate solutions as a novel route for the generation of highly performing large-area anti-reflective (AR) surfaces on glasses for solar energy conversion. Compared to alternative technologies, the present approach enables processing at very low cost. The mechanism of coating formation and consolidation was evaluated. Following deposition, the aqueous potassium silicate solution dries into a gel of interconnected SiO_2 colloids and dispersed potassium hydroxides and carbonates. A typical size of ~20–40 nm of the colloids is established already at this stage without significant growth in the later process. Potassium species are removed in a subsequent washing procedure, leaving only a minor amount of residual potassium at the interface between coating and substrate in an otherwise nanoporous silica layer. Physically and chemically bound water species are driven-out of the coating in a final annealing step. In this way, an AR layer of nanoporous silica with a thickness of ~100–150 nm is easily created. The AR effect is caused by two-beam interference at this layer, enabling an absolute transmission increase of 3.6% at a wavelength of 550 nm and a relative transmission increase of 3.1% over the spectral range of 400–1100 nm for a single-side coating on solar glass for c-Si as well as thin-film modules.

1. Introduction

Decreasing the reflection losses at material interfaces represents one approach for increasing the efficiency of photovoltaic (PV) modules [1] and other systems for solar energy conversion [2]. Today, optical loss from state-of-the-art glass covers is in the range of 8% [3], resulting primarily from Fresnel reflection and hence, dependent on the angle of incidence of the incoming light. Reflection from an unmodified silicon cell is in the range of 36–37% [4,5] when averaged over all angles of incidence [5]. Various types of coatings and surface treatment procedures are usually employed to reduce the reflection loss from the active components of the system (solar cells, thermal collectors, etc.) to a range of ~10–12% for commercially available components, and down to ~6–7% [5] or even lower [2] in the development stage. On the other side, also the reflection loss caused by the cover glass (i.e., on the module-level) cannot be ignored. In many cases, it is even more readily accessible than the active components and therefore presents an effective property for leveraging module efficiency. Efficiency, in the application-oriented context, is typically defined as cost-per-Wp [6]. Commercial photovoltaic energy conversion has presently reached a value of roughly 0.8 (thin film)–1.0 (c-Si) US$/Wp [7], dependent on cell technology. Here, a significant part of overall cost (typically 20–30%) is caused by the employed glass material [8]. In view of further cost reduction, cost-effective improvement and/or functionalization of PV cover glasses therefore become/becomes particularly important. For example, a share of ~30% (or ~50%) is projected for anti-reflective (AR) glass in c-Si (or thin-film) solar modules by 2015.

Glasses with reflection-controlling coatings are well known and commercially available [4]. They comprise tailored broad or narrow band UV, VIS and/or IR reflection or antireflection properties for various applications [9]. However, most fabrication processes cannot be directly transferred to solar glasses because of cost, mechanical stability and bandwidth. In solar energy conversion, commercially available [10,11] coating solutions appear to be advantageous in PV systems [10,12–14], concentrated solar power [15], solar thermal collectors [1,15–17] and hybrid systems [11]. These coatings typically rely on formation of an effective optical medium [18] of low refractive index at the glass surface, which is obtained by depositing a nanoporous silica layer [10,16,19]. That is, for a typical cover glass sheet with refractive index n~1.52, optimal broadband AR is obtained for a layer with a thickness of $\lambda/4$ at the desired peak transmission wavelength λ (e.g., 150 nm for

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$\lambda = 600$ nm) and sufficiently low refractive index, according to Fresnel's law optimally $n_{coat} \sim 1.23$ for normal incidence. State-of-the-art nanoporous silica layers with a porosity of ~50%, in theory, reach a value of $n_{coat} \sim 1.23–1.26$, resulting from the refractive index of silica of 1.46. It must be assumed, however, that this optimal value is strongly affected by, e.g., capillary condensation, corrosion, interdiffusion and corrosion-induced carbonation and various other effects which occur in real-world and long-term exposure.

AR coatings for solar glasses described in the scientific literature are often created via sol–gel processes using tetraethylorthosilicate (TEOS) or a prefabricated silica sol [4,7,17]. For example, a peak transmission of 99.1% has been reported for a commercial both-side antireflective coating on solar glass [10]. The porous silica layer may be manipulated to obtain improved mechanical properties [20] or other functionalities such as anti-soiling [17]. Other techniques to obtain AR surfaces for PV applications comprise surface etching [11], vapor deposition processes [12] or polymer deposition [13]. As of today, the most critical limit of all these approaches is the trade-off among optical performance, mechanical (abrasion, scratch) and chemical (corrosion) resistance, and cost of the obtained AR layer, especially in view of the required 20 or more years of lifetime.

In this paper, we report an alternative way to generate, at low cost, large area AR coatings on glass with improved adhesion and high performance. The approach relies on wet (spray- or dip-) deposition of aqueous potassium silicate solutions which are then transformed into nanoporous silica layers. Such aqueous silicate solutions, also referred to as '*water glass*' [21,22], are widely applied materials in as different fields as painting technology, oil recovery and cosmetics. Water glass is a relatively cheap material produced through dissolution of alkali silicate glass at elevated temperature and pressure to yield alkaline aqueous solutions of anionic silicate species. From the chemical viewpoint, it is a very complex dynamic system of dissolved silicates from molecular [23] to colloidal [24] length-scale with varying configurations. In analogy to silicate glasses, their structure can be described via the alkali-to-silica ratio, from which results a specific degree of polymerization of $[SiO_4]^{4-}$ tetrahedra [25,26]. While sodium silicates are well described, potassium silicates appear to have seen less research [27]. As coating material, soluble silicates have been applied as binder materials for pigments and phosphors on CRT-TV-screens [28], flame-retardant coatings [29] and protective coatings on metals [30]. Sodium or potassium silicates have also been suggested as antireflective and anti-glare agents [31]. A thin aerogel film derived from a sodium silicate solution on a glass plate was shown to increase optical transmission by 5–8% [32], but by applying ion exchange in a time consuming process.

2. Experimental

2.1. Coating procedure

The general procedure of coating deposition and consolidation is shown in Fig. 1. Aqueous potassium silicate solutions were wet-deposited on commercial soda lime silicate float glass sheet by either dip or spray coating. It is important to note that the two faces of float glasses exhibit distinct chemical properties, resulting from the in-diffusion of tin on the side which was in contact with the tin bath during the floating process. If not stated otherwise, in the following, we consider always the air-side (tin-free) of the glass. We will primarily discuss laboratory tests of dip-coated samples on which a precursor solution with a silica modulus SiO_2/K_2O (wt%) of 3.83 and a nominal concentration of solids of 5 wt% were deposited. Precursor liquids were obtained from BASF, Germany, and used as-received. Before coating, glass substrates were pre-conditioned by washing in distilled water and acetone and subsequent plasma treatment for 120 s (air, PLASMAclean 4, Ilmvac, Ilmenau, Germany) to improve surface wetting. Three different extraction speeds were used for dip-coating, 0.9; 1.8 and 3.8 mm/s. A dipping angle of 90° was employed. After coating, the glasses were dried at room temperature in ambient atmosphere for ~5 min and subsequently rinsed in distilled and de-ionized water. Finally, the samples were heat treated at 500 °C for 22 min followed by natural cooling in an electric muffle furnace (LM312, Linn High Therm, Eschenfelden, Germany).

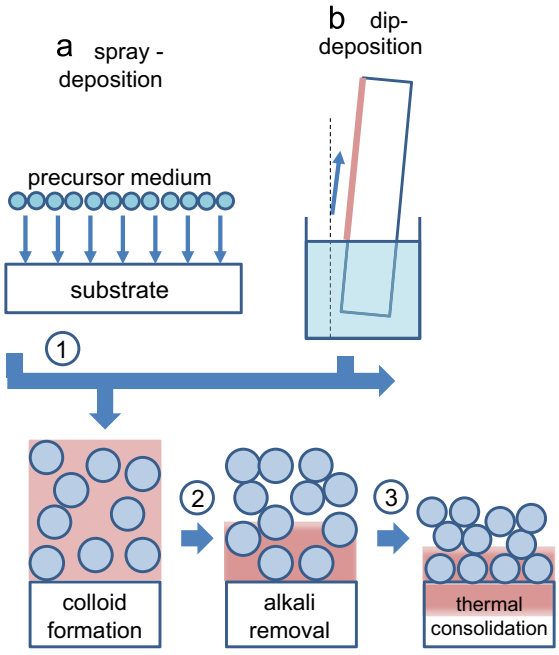

Fig. 1. Schematic of the process of coating deposition and consolidation, comprising wet deposition by either spraying (a) or dipping (b). The final AR film is generated during a procedure of drying and formation of a sol (1), washing and potassium removal (2) and thermal annealing (3).

2.2. Characterization

All analyses were performed over the different stages of the process of coating deposition and consolidation with the objective to evaluate coating performance and consolidation mechanism. UV–NIR transmission spectra were recorded over the spectral range of 170–2500 nm (Lambda 950, Perkin-Elmer, Unterhaching, Germany). The effective refractive index at 632.8 nm and the thickness of the coatings were estimated by ellipsometry (EL X-02C, Dr. Riss Ellipsometerbau, Ratzeburg, Germany).

Direct measurements of surface topology were conducted by atomic force microscopy (tapping mode AFM, Multimode, Digital Instruments, Santa Barbara, USA), using a silicon tip with a nominal radius of 10 nm (NSC35, μMasch, San Jose, USA).

Chemical depth profiles perpendicular to the coating–glass-interface were recorded by secondary neutral mass spectroscopy in a Kr plasma at Clausthal University of Technology (SNMS, INA-X, Specs, Berlin, Germany). For that, additional coating samples were produced on soda lime silicate float glass with an extraction speed of 0.9 mm/s. Chemical profiles were taken on the tin-side of the substrates. The average sputter rate was in the range ~0.3 nm/s over approximately 1700 s (i.e., to a depth of ~550 nm). These samples did not see a thermal treatment in order to obtain