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Super-durable closed-surface antireflection thin film by silica nanocomposites

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ABSTRACT

A closed-surface silica antireflection thin film was prepared in single dipping process by growing branched silica chain from modified acid catalyzed sol-gel in hollow silica sphere sol-gel. The refractive index and thickness of thin film could be fine-tuned via acid catalyzed sol-gel content and withdrawing speed. Transmittance of this closed-surface AR thin film was as high as 97.1% with refractive index around 1.25–1.27. 2.5% gain in short circuit current was measured from both external quantum efficiency and flashing test on mini photovoltaic modules. The closed-surface structure was with a 5 H pencil hardness, and approximately 2.0 GPa indent hardness in nanoindenter test. It was resistant to high moisture and high temperature, mainly due to absence of voids on surface. The closed-surface AR thin film had potential to be applied in photovoltaic module, architecture windows in severe climate conditions.

1. Introduction

Antireflective (AR) thin film is a vital component in optical devices, which has been attracting much attention for their applications in display devices, architecture windows and photovoltaic (PV) modules as a result of its capability of light harvest [1–4]. Generally, AR properties are the results of destructive interference between light reflected from the coating-substrate interface and the air-coating interface [5]. For a given wavelength, under the condition of quarter-wave layer thickness ($\lambda/4$) of a coating material, minimum reflection can be achieved when refractive index (RI) of coating material is equal to the square root of the substrate's RI [6]. For photovoltaic glasses, which having a RI around 1.52, the RI of a quarter-wave AR thin film should be approximately 1.23, which is far below the lowest RI of any dense material (MgF_2: 1.38).

However, according to Yoldas, RI of porous SiO_2 thin film can be manipulated varying from 1.1 to 1.5, because the inner cavities of porous SiO_2 thin films offer a large volume for tuning the RI [7]. This allows the deposition of SiO_2 AR thin films even on a substrate with a low RI, like PV glasses. Several papers have already demonstrated how the deposition of a porous SiO_2 AR thin film on PV glasses to improve transmittance, thus to increase module peak power [8,9].

For products intended as outdoor applications, such as PV glasses and architectural windows, environment durability of AR thin film is as important as its optical properties [10]. The porous AR thin films usually suffer from poor mechanical properties and functional durability because nano-particles are bonded to each other and to the substrate only by van der Waals forces [11]. Moreover, the porous surface of AR thin film is prone to absorb water and contaminants in the field, which give rise to the variations in the RI and degradation of the transmittance [12,13]. These two factors have been preventing the practical use of porous AR thin film in severe climate conditions.

Porosity more than 40% must be preserved in SiO_2 AR thin film to achieve low RI around 1.23. It is highly challenging to design and fabricate such a highly porous SiO_2 AR thin film with good mechanical properties. Sun et al. reported replacing amorphous SiO_2 by zeolite to increase hardness of thin film, zeolite film having 1.5 GPa indent hardness and 35 GPa elastic modulus was obtained, but transmittance of zeolite thin film became substantially lower [14]. Boilot et al. suggested that an alternative solution could be to transform the open surface porous thin film into closed-surface thin film with hollow nanospheres (HN) in the range of 30–100 nm, thus avoiding the adsorption of moisture and structure network dissolution [15]. Cohen et al. fabricated both closed-surface and open surface SiO_2 AR thin film using layer-by-layer (LBL) dip-coating, but these materials produced a significant reduction in the transmittance from the visible to the near-infrared regions [16,17]. Zhang et al. infiltrated acid catalyzed silica into voids of porous SiO_2 AR thin film to produce a closed-surface thin film,

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and achieved a weather resistible AR thin film on PV glass with transmittance of 96.9–97.3% [18]. While, this method needed at least 2 steps of coating processes, which made the processing complicated and hard to be implemented in practice.

In this study, we proposed a single dipping sol-gel contented SiO_2 HNs with silica from a modified acid catalyzed hydrolysis grew on these SiO_2 HNs. The branched chain structured acid catalyzed silica was used as a binder to link SiO_2 HNs to each other as well as to the substrate to improve mechanical properties of thin film. The acid catalyzed silica was also used to block voids on the surface to prevent water and contaminations penetrating into the thin film, thus improved the outdoor reliability performance. By optimizing the porosity of closed-surface AR thin film, a super weather resistible AR thin film was obtained, which can be used in photovoltaic modules, architecture windows and other outdoor applications.

2. Experimental section

2.1. Materials

Tetraethylorthosilicate (TEOS, 98%), ammonium hydroxide (NH_3, 8–28%), hydrochloricacid (HCl, 8%), absolute ethanol (EtOH, 99.5%), 3-Aminopropyltriethoxysilane (APTES, 98%) were purchased from Sinopharm. Poly acrylic acid (PAA, 30 wt% in water, Mw = 3000) was purchased from Macklin. All chemicals were of analytic grade and used without further purification. Deionizer (DI) water with a resistivity no less than 18.2 MΩ·cm was used in all experiments. 2 mm-thick K9 glasses from Shanghai Jijia Optical Instrument Co. ltd. were used for optical characterization, 3.2 mm-thick low iron PV glasses, purchased from Flat Co. ltd. with a patterned rear side, were used for making mini modules and reliability test samples.

2.2. Preparation of sols

Step a, 1.18 g of PAA was first dissolved in 22 mL aqueous ammonia, this solution was subsequently mixed with 440 mL of absolute ethanol under vigorous magnetic stirring.

Step b, under vigorous magnetic stirring at room temperature, 5 aliquots of TEOS totaling 11 mL were injected into this solution, the aliquots were added at intervals of 1 h. After 12 h, 40–50 nm SiO_2 hollow nano-spheres were formed. Subsequently, ammonia was removed by refluxing the sol-gel at 80° for 6 h in a ventilating cabinet. This was followed with a condensation of the sol-gel to a target solid content of approximately 3%.

Step c, 12 mL TEOS, H_2O, HCl and ethanol were subsequently added into condensed HNs solution, with the molar ratios of TEOS: HCl: H_2O: EtOH = 1: 0.2: 12: 23 under vigorous stirring for 4 h. 3 aliquots of APTES totaling 14 mL were injected into mixed sol during stirring, the aliquots were added at intervals of 1 h. The sol-gel was then aged for 5 days in room temperature to allow TEOS react. The scheme of reaction process was showed in Fig. 1.

2.3. Fabrication of closed-surface SiO_2 AR Thin films

The glass slides were first washed using detergent, followed by ultrasonic cleaning in DI water for 10 min and subsequently followed by flushing of ethanol. The cleaned glasses were immersed in AR sol-gel for 30 s, and withdrew from the sol at 1.0 mm/s, followed by drying in the air for 10 min at room temperature. Finally, the PAA template and other organics were removed via calcination in air (conducted in a muffle furnace at 550 °C for 2 h) to form the closed-surface AR thin films. Open surface control samples of solo SiO_2 HNs AR thin film were fabricated on glass substrates using silica sol from step b, its calcination was performed at the same temperature.

2.4. Characterization of Microstructure and Morphology

Scanning electron microscopy (SEM) observations were conducted in a Supra-12 field emission scanning electron microscope. The cross-section samples were prepared by mechanically breaking of calcinated samples. Both cross-section and surface morphology samples were coated with gold film in an ion sputtering before SEM characterization. For transmission electron microscopy (TEM) observations, sols were diluted in ethanol by sonication for 15 min, followed by adding onto carbon-coated copper grid and dried in air, they were observed using a JEOL JEM-2100 transmission electron microscope at an acceleration voltage of 150 kV. The roughness and morphology of thin film surface were characterized by atomic force microscopy (AFM) using a Nanoscopy IIIa scanning probe microscope.

2.5. Optical characterization

Spectral was measured in the wavelength range of 300–1200 nm that covers both UV–vis–NIR region for PV modules and the visible region for architecture windows. Transmittance curve in this range were measured with a Varian Cary 5000 UV–vis–NIR spectrophotometer, with scanning step size of 5 nm. Refractive index and AR thin film thickness were determined by an ellipsometer model Semilab SE 1000.

2.6. Module external quantum efficiency and flashing measurement

External quantum efficiency (EQE) was conducted by Bentham PVE300-IVT, on laminated single solar cell (156×156 mm^2) mini PV modules, also measured in the wavelength range of 300–1200 nm. Flashing test was conducted on the same samples under the standard test condition (STC, 25 °C, 1000 W/m^2) by Halm IV tester with a Xe bulb which can generate an AAA AM1.5 spectra (IEC60904).

2.7. Reliability evaluation

The reliability performances were evaluated by damp heat (DH) test. In damp heat test, samples were put into a chamber with 85 °C and 85% relative humidity for 1000 h or even longer, no visual degeneration was allowed after the test. Espec AR climate chamber was used to conduct the damp heat test in this study.

2.8. Detection of mechanical properties

A nanoindenter (NANO G200, MTS) was used to determine the elastic modulus and hardness of thin films. Before performing any indentation, the indenter was stabilized so that the thermal drift rate was less than 0.05 nm/s. For all indentations, a constant strain rate (0.05 /s) loading was used. For each sample, 10 points were measured and statistically analyzed. The mechanical strength of thin film was evaluated by pencil scratch hardness test (ASTM D3363-92a). The pencil hardness was determined by the hardest pencil that will not leave a visible trace on the AR thin film when viewed at an oblique angle.

3. Results and discussion

3.1. Morphology and structure of closed-surface AR thin film

Many synthetic methods have been developed to synthesize SiO_2 HNs recently [19,20]. In this synthesis protocol, PAA was added into ethanol to form nano-scale PAA spheres. These nano-scale spheres were used to be the core templates to be enclosed by silica from hydrolysis of TEOS, and removed later by calcination. The ratio of PAA to ethanol determined the PAA core size, and the silica shell thickness was controlled by the injection amount of TEOS. The mean diameters of PAA core were 40–50 nm, and silica shell thicknesses were 6–10 nm in this