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Short communication

Preparation of antireflective SiO_2 nanometric films

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Abstract

Antireflective nanometric SiO_2 films were formed on glass substrates by dip coating from a colloidal SiO_2 sol having an average particle size of 9 nm. Withdrawal speed of dip coating was varied between 100 and 200 mm/min with 25 mm increments, and baking temperature of the films was altered between 300 and 550 °C with 50 °C increments. Obtained SiO_2 films were in 80–200 nm thickness range. Film thickness was seen to increase with increasing withdrawal speed and to decrease with increasing baking temperature. A maximum light transmittance of 95% was obtained with 4.5% points increase, from the films which were withdrawn at 100 mm/min and baked at 450 or 500 °C. It was seen from SEM observations that the films exhibited full coverage on glass surface and contained no voids or cracks. Size of SiO_2 particles in the film was seen in the AFM analyses to increase with baking temperature. Sintering of SiO_2 particles appeared to accelerate at temperatures over 450 °C.

Keywords: A. Sol–gel processes; C. Optical properties; D. SiO_2; Nanometric film

1. Introduction

Antireflective (AR) films, which reduce the reflective losses of light, have been used in applications such as shop windows, video display panels, cathode ray tubes and solar panels [1–4]. Solar power application group consisting of solar thermal systems and photovoltaics is one of the widest markets for AR coated glasses. Display devices, on the other hand is the other growing market for AR glasses, as a result of increasing conventional utilization of new display technologies such as LCD or LED screens that are becoming cheaper.

There are mainly two methods for obtaining AR surfaces on glass. One is based on chemical etching of glass surface [5]. Etching basically is removing leachable components from the glass surface, thereby leaving a skeletonized porous surface with a lower refractive index than the glass itself. Involvement of hazardous acid etchants and the necessity to soak the glass at ~630–660 °C before etching in order to create a phase separation on the surface may be mentioned as the disadvantages of this process [5]. The second method is essentially forming a coating layer with a low and adjustable refractive index on the glass surface, by various means such as CVD, sol–gel and sputtering. Among the techniques of obtaining thin films on glass surface, sol–gel process comes out as a versatile method with its high process speed, suitability for continuous production and variety of chemical precursors. As compared to conventional coating methods, the most important advantage of sol–gel processing is the possibility of precise control on the microstructure of the deposited film, such as the pore volume, pore size and surface area [6]. Additionally, the low cost of sol–gel method is another important reason for its wide practice [7].

Among the commonly used AR coatings, SiO_2 stands out due to its low refractive index of 1.45, good environmental stability and durability. Thus, in the second method generally porous silica is utilized. Studies have focused on controlling of porosity, in order to adjust the refractive index of the SiO_2 films. Vincent et al. studied on tetraethylortosilicate (TEOS) to base molar ratio and reported that the mean particle size and also pore size increased about threefold when TEOS to base molar ratio was increased from 1:1 to 1:3 [8]. In the study of Yoldas

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[9], alkoxide and water ratio was changed for adjusting the porosity. Wu et al. [10] proposed a novel two-step acid-base catalyzed preparation method for controlled refractive index. In this method, HCl and NH_3 catalyzed SiO_2 solutions were prepared separately and then the two sols were mixed. Another approach of controlling the refractive index of the film, as proposed by Tong et al. is to utilize multiple layers of SiO_2 where refractive index of each layer decreases towards the outer layer of the coating, with increasing particle size [11]. Wongcharee et al. [12] investigated preparation of a porous SiO_2 films by adding pore creators into the sols such as polyethyleneglycol (PEG). One reported drawback of pore creator addition is the resulting poor mechanical properties of the SiO_2 film [13].

Porous SiO_2 films have previously been reported to be synthesized through sol–gel by using mostly TEOS [8,14,15]. In this work, SiO_2 films were obtained on soda-lime glass surfaces by dip coating, using SiO_2 sols prepared from tetramethoxysilane (TMOS). In order to investigate the effects of withdrawal speed and baking temperature on the thickness of SiO_2 films and light transmittance of glass, withdrawal speed was varied between 100 and 200 mm/min with 25 mm increments and baking temperature was altered between 300 and 550 °C with 50 °C increments.

2. Experimental procedure

SiO_2 sol was prepared by hydrolysis and polymerization reactions of tetramethyl orthosilicate (TMOS, Fluka Chemicals, >98%) in the presence of nitric acid catalyzer (HNO_3, Merck Chemicals, 65%). TMOS:HNO_3:H_2O:EtOH were mixed in required amounts with a molar ratio of 1:0.55:7.54:6.46. The mixture was stirred at 70 °C on reflux for 20 h. The obtained sol, containing 9.7 wt% SiO_2, was diluted with EtOH at one third ratio, resulting in a SiO_2 content of 3.23 wt%. Obtained sol was used for dip coating after an aging period of 24 h.

Particle size distribution of the SiO_2 sol was determined by a particle size analyzer (Zetasizer Nano-ZS, Malvern Instruments). 4 mm thick, 10 cm × 15 cm soda-lime glass substrates were coated by dipping them into the SiO_2 colloidal sol and withdrawing at 100, 125, 150, 175, 200 mm/min speed. After drying in air at room temperature, the coated glass samples were baked at 300, 350, 400, 450, 500, 550 °C for 1 h.

Glass samples containing nanometric SiO_2 films were subjected to optical and morphological analyses. Light transmittance was measured by a hazemeter at 550 nm (Haze-Guard Plus, BYK Gardner) and percent light transmittance increases provided by the SiO_2 films were determined. Scanning electron microscopy (SEM) analyses were performed with a Zeiss Leo 1430 unit. For atomic force microscopy (AFM) analyses a PSIA XE-100E unit was utilized. Root mean square (rms) surface roughness was evaluated from the AFM line profile data by XEI software (PSIA Inc.). Film thicknesses were determined by Filmetrics F20-HC thin film measurement system, precision of which was specified as 1 nm by the manufacturer.

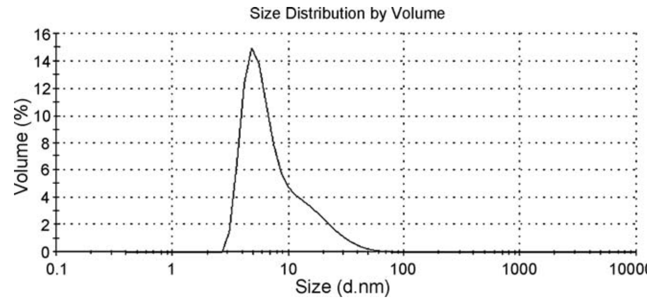

Fig. 1. Particle size distribution of SiO_2 sol.

3. Results and discussion

Average particle size of the SiO_2 colloid was determined as 9 nm by particle size measurement. Particle size distribution graph of SiO_2 sol is given in Fig. 1. The employed method appears to be suitable for obtaining nano-size SiO_2 particles.

In dip coating process, higher withdrawal speeds result in thicker films as compared to lower speeds, due to the increase in upward viscous drag on the liquid by the moving glass substrate [6]. Variation of SiO_2 film thickness by withdrawal speed for the samples which were baked at 500 °C for 1 h is presented in Fig. 2. At speeds of 100–125 mm/min, the formed film has a thickness of about 100 nm, and thickness of the film increases with increasing withdrawal speed. At 200 mm/min speed, a SiO_2 film with a thickness of 150 nm is obtained.

Change in SiO_2 films thickness relative to baking temperature can be seen in Fig. 3. The withdrawal speed of these films was fixed at 100 mm/min and baking duration was 1 h. At baking temperature of 300 °C the film thickness is around 120 nm and it is seen to decrease to about 100 nm with increasing temperature up to 500 °C. The decrease in the film thickness is more pronounced when baking temperature is raised from 500 to 550 °C. After baking at 550 °C for 1 h the SiO_2 film thickness was measured as 80 nm. This result can be taken as an indication that the degree of sintering is higher after 500 °C as compared to below 500 °C.

Variation in the light transmittance increase of SiO_2 coated glasses as a result of change in withdrawal speed during dip coating and as a result of change in baking temperature of SiO_2 films are presented in Table 1. The highest light transmittance values are obtained when withdrawal speed is 100–125 mm/min and when baking temperature is 450–500 °C. Light

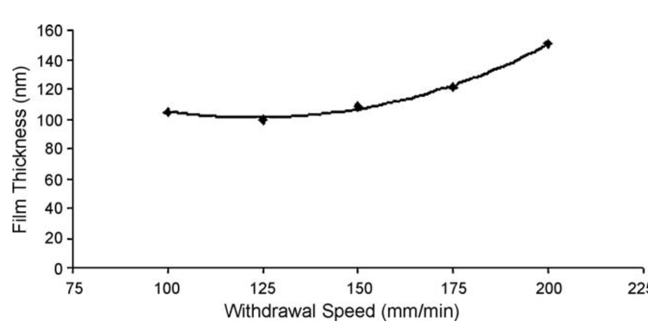

Fig. 2. Variation of SiO_2 film thickness by withdrawal speed (baking temperature 500 °C).