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Fabrication of antireflective antifogging nano-porous silica thin film on glass substrate by layer-by-layer assembly method

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ABSTRACT

In this research, silica nano-porous thin films were deposited on glass substrates by layer-by-layer assembly process. The structure, morphology, surface characteristics, surface roughness, and optical and hydrophilic properties of the thin film were investigated. The X-ray diffraction analysis shows that the silica nano-porous thin film has an amorphous structure. The transmittance spectra revealed that the silica nanoporous thin film increased transparency of the glass substrate from 91.8% to 97% at 550 nm. In addition, the silica nanoporous thin film decreased water contact angle of glass surface from 67° to 3°. Therefore, silica nanoporous thin film showed high transparency and superhydrophilicity which greatly encourage the antireflection and antifogging functions of the thin film.

1. Introduction

Antireflective antifogging thin films can effectively enhance the light transition and prevent ghost images in optical surfaces. In recent years, smart materials such as antireflective antifogging thin films have attracted intensive attention in especially appellations such as eyeglasses, swimming goggles, periscopes, and lenses in endoscopic surgery [1–3].

The antireflection principle is based on the destructive interference between light reflected from the air-film and film-substrate interfaces [4]. Generally, a single thin film with an appropriate refractive index can be utilize as an antireflection coating for glass substrate which should fulfill two statuses: (1) the thickness of the thin film should be $\lambda/4n_c$, where λ is the wavelength of the incident light; (2) the refractive index of the thin film should be $n_c = (n_a n_s)^{1/2}$ where n_c, n_a and n_s are the refractive indices of the thin film, air and substrate, respectively. For a glass substrate ($n_s = 1.5$), the refractive index of the antireflection thin film according to condition (2) should be ~1.22. However, optical materials with such low refractive index are either scarce or costly to generate in thin film form. As a substitution, nano-porous optical materials can be selected as antireflection coatings, since the insertion of the nano-pores can decrease the refractive index of the coatings and fulfill the antireflection requirements [5–8]. Also, the pores of the coating must be small enough to prevent the incident light scattering. In nanoporous materials, the pore sizes in the coatings for antireflection properties in the visible wavelengths must be smaller than 50 nm [9].

The antifogging effect of the thin films has been ascribed to superhydrophilicity. The superhydrophilicity of the thin film surfaces allows the water to spread across the surface rather than remaining as water droplets, thus making the surface anti-fogging. In recent years, transparent antifogging TiO_2 thin film on glass substrates has a high potential for practical applications such as mirrors, window panes and automobile windshields [10,11]. However, TiO_2 thin film only exhibits superhydrophilicity under UV light irradiation. In practical applications, UV irradiation light on the TiO_2 surface does not always occur [1]. Therefore, it is preferable that the thin film obtains its super-hydrophilicity without UV irradiation. It is observed that textured surface induced superhydrophilicity without UV irradiation. Such superhydrophilic surface structures have been created by lithographic patterning techniques or by formation a porous structure by creation of surface roughness. Surface roughness will perform the hydrophilic surface material more wettable [12]. Then, it is possible to achieve superhydrophilicity by incorporation of nanoporous into hydrophilic coatings. Therefore, it is expected that highly porous antireflection coatings made from hydrophilic materials could be superhydrophilic and possess the antifogging property.

In recent years, it is observed that silica nano-porous coating can show superhydrophilicity and the antifogging effect without UV irradiation. The silica nano-porous thin films can be fabricated by various methods such as sol–gel process, phase-separation, layer-by-layer (LbL) deposition method, and plasma-enhanced chemical vapor deposition. Among these methods, the layer-by-layer method (LBL) is a desirable technology for fabrication of silica coatings since it allows deposition of coatings on large area, non-flat surfaces and wide range of substrates [13–16]. In this study, the silica nano-porous thin film

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was deposited on glass substrates using LbL assembly method. Then, the superhydrophilicity, antifogging effect and antireflection properties of the silica nano-porous thin films were investigated.

2. Experimental method

2.1. Materials

Polycation poly(diallyldimethylammonium chloride) (PDDA, 20 wt.%, *M*w ca. 100,000–200,000), poly(acrylic acid) (PAA *M*w ca. 100,000), and sodium silicate solution (reagent grade) were all purchased from Sigma-Aldrich and used as received. Distilled water was used throughout the experiment; soda-lime glass slides with a thickness of 1.0 mm were utilized for film deposition.

2.2. Preparation of PDDA and sodium silicate complexes

An aqueous solution of PDDA (2.0 mg/mL) was added dropwise to aqueous sodium silicate (68.8 mg/mL) under stirring. The ultimate volume ratio of PDDA and sodium silicate solutions was 60:15. The pH value of the aqueous PDDA–silicate complex solution was adjusted to 4.0 by using 1 M HCl.

2.3. Fabrication of the silica nanoporous thin film

The glass slides were first immersed in a (2 mg/mL) PDDA solution for 10 min to give the substrate positively charged and then rinsed with water and dried with a heater. Then multilayer films of PAA/PDDA–silicate were immobilized on the glass substrates according to the following general steps: (a) the glass substrates were immersed in a solution of PAA (1.0 mg/mL, pH 4.0) for 5 min, followed by rinsing with water and drying with heater. (b) The substrates were immersed in a solution of PDDA–silicate complexes for 20 min, followed by rinsing with water for and drying with heater. Steps (a) and (b) were repeated until the desired number of deposition cycles was reached. Multilayer films of the PAA/PDDA–silicate with *n*-cycle deposition is noted as $(PAA/PDDA–silicate)_n$, where n is 12 in this study. Finally, the coated slides were calcinated at 300 °C for 4 h at air atmosphere.

It is necessary to mention, that before coating, the soda-lime glass slides were dipped in a slightly boiled mixture of 98% H_2SO_4 and 30% H_2O_2 (piranha solution), for 10 min and then rinsed with water and dried to improve the adhesion of the coatings onto the glass substrates.

2.4. Characterization

The structure, morphology, surface characteristics and surface roughness of the thin films were determined using a Bruker X-ray diffractometer (D8ADVANCE, Germany, Ni-filter, Cu Kα radiation λ = 1.5406 °A, grazing angle), field emission scanning electron microscopy (FE-SEM, Hitachi S4160, cold field emission, voltage 20 kV), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR; Bruker Germany, Tensor 27, resolution of 4 cm^{-1}, scanning speed of 2 mm/s) and atomic force microscopy (AFM, Veeco CPR USA contact mode), respectively.

The transmittance and reflectance spectra of the thin films were obtained using a UV–VIS–NIR spectrophotometer (Shimadzu UV-3100) at normal incidence in the wavelength between 300–800 nm. The superhydrophilicity of the thin films was evaluated by measuring the contact angle of a water droplet on the film surfaces. A droplet was injected on to the surface using a 1 μL micro-injector. The water contact angle was averaged from five measurements.

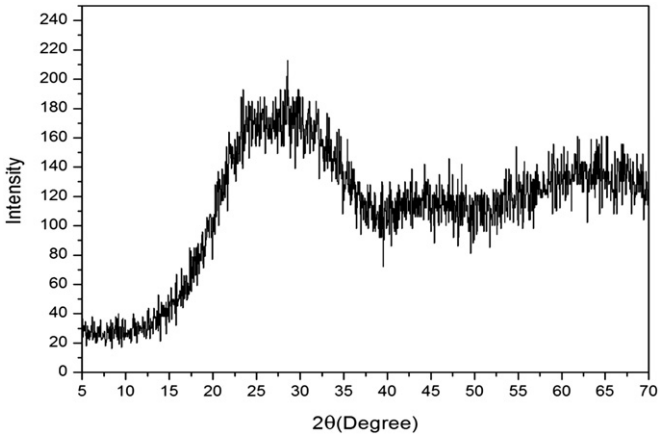

Fig. 1. XRD pattern of the silica nano-porous thin film.

3. Results and discussion

The XRD pattern of the silica nano-porous thin film is shown in Fig. 1. The XRD measurement shows that the thin film has an amorphous structure.

Fig. 2 shows the ATR-FTIR reflection spectra of the silica nanoporous thin film. The characteristic bands almost at 1087 cm^{-1} and 805 cm^{-1} correspond to the stretching and bending of Si–O bands, respectively [17]. The position and the shape of the Si–O vibration band at 1087 cm^{-1} shows a stoichiometric silicon dioxide structure which indicated on amorphous silica [17]. ATR-FTIR result indicates that calcinations at 300 °C not only removed the organic components, but also cross-linked the silicates together by formation of the stable (Si–O–Si) bands among them in the coatings. The highly cross-linked film structure greatly improves the adhesion of the silica nanoporous thin film to the glass substrate.

Fig. 3 shows the FE-SEM image of the silica nanoporous thin film. It can be seen that the calcinated $(PAA/PDDA–silicate)_{12}$ thin film is highly porous. Nano-pores with sizes between 30 and 80 nm are clearly observed for the film which was calcinated at a temperature of 300 °C. These nano-pores were formed during burning of PDDA and PAA organic components in calcination process. FE-SEM image reveals that the calcinated coatings are composed of loosely stacked silica nanoparticles. The silica nanoporous thin film due to small pore sizes, in comparison to the micro-porous thin films, does not scatter light [9]. Then, it is possible to use as an antireflection coating which is discussed in the following.

AFM was used to characterize the surface roughness of the bare glass and silica nanoporous thin film coated glass. Fig. 4 shows AFM images of the bare glass and silica nanoporous thin film coated glass. The root mean square roughness values (Rrms) of the bare glass and silica

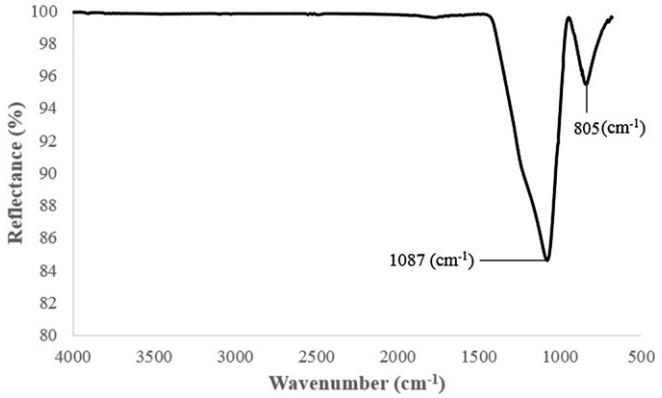

Fig. 2. FTIR-ATR spectra of the silica nanoporous thin film.