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Single-layered porous silica films on polyethylene terephthalate substrates for antireflection coatings

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ABSTRACT

Single-layered porous silica films were prepared on polyethylene terephthalate (PET) substrates as antireflection coatings for efficient, large-scale flexible optoelectronic devices. Cetyltrimethylammonium bromide (CTAB)-templated synthesis was employed to form porous silica films. Without using high temperature treatment, CTAB was removed by washing in water to create a porous structure in the films. To spin-coat on PET substrates, contact angle between silica sol and PET surface was measured to optimize the molar ratio of the solution. Pore size and surface sharpness were estimated using atomic force microscope data. The average reflectance of as-prepared AR coatings on PET substrates was ≤2%.

1. Introduction

Antireflection (AR) coatings are widely used for various optical applications, such as displays, lenses, and solar cells. In general, multilayer has been employed to achieve an antireflective effect over a wide wave length range. However, this method is not straight forward and cost-effective because of its complex process of fabrication. In 1999, high-performance antireflection coating with single layer on glass substrates was developed by Walheim [1]. The reflectivity of single-layered AR films can be reduced if they obey Fresnel's equation.

$$n_1 = \sqrt{n_0 n_s} \quad (1)$$

where n is refractive index, and subscripts 1, 0, and s refer to the film, air and substrate, respectively.

To obtain single-layered films with a desired n_1, pores should be formed in the film. There have been numerous studies on AR coating with single layer [2–8]. One of them is Moth's eye structure, which has ideal reflection characteristics over a broad range of wavelengths [4–8]. This technique is difficult to apply on large and flexible substrates, though. In other way, the sol–gel method is used to synthesize porous thin films for antireflective applications [9]. Cetyltrimethylammonium bromide (CTAB) was usually employed as a surfactant to make micelles so that nanometer-size pores can be formed in the silica films after the subsequent decomposition of the micelles at high temperature. In this case, microstructures of silica films are mainly determined by the chemical composition of sols. Lamellar, 2D-hexagonal and 3D-hexagonal arrangements are obtained at different molar ratios (MRs) of CTAB/Si [10,11].

Here, we introduce a simple low temperature-method of preparing single-layer AR films on large flexible substrates. Single-layered silica films were fabricated on polyethylene terephthalate (PET) substrates using the CTAB-templated process, which can be compatible with flexible displays and photovoltaic devices. High-temperature treatment for pore formation is difficult on flexible substrates, so AR films were prepared using washing at low temperature.

2. Experimental details

2.1. Preparation of solutions

The chemicals used in making solutions were tetraethylorthosilicate (98%, Acros), ethanol (absolute, J.T. Baker), CTAB (Sigma-Aldrich), hydrochloric acid (HCl 36%, Sigma-Aldrich), and distilled

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water (dH_2O). Solutions were prepared by mixing 0.327 g of CTAB and 76 g of ethanol in a 250-ml three-neck flask equipped with a condenser, and stirring for 1 h. Then the flask was filled with N_2 and 6.25 g of tetraethylorthosilicate (TEOS) was added. Then 2.7 g of HCl aqueous solution was diluted with dH_2O and added into the mixture. Finally, the mixture was heated to 80 °C and stirred for 2 h. The MR of TEOS:CTAB:ethanol:dH_2O:HCl was adjusted to be 1:0.03:55:5:0.004 for spin-coating on the PET substrates.

2.2. Preparation of antireflective films

PET films are very flexible, so direct sol–gel spin coating on them can be difficult. Therefore, adhesive undercoated PET films (Hostaphan® 2600 PET films, Mitsubishi Polyester Film Inc., reflectance 7.18%, haze 4.5%, density 1.395 g/cm^3) were attached to glass substrates before single-layered AR films were coated on the PET. AR solution was spin-coated at 1000 rpm. The samples were baked at 100 °C for 5 minutes on a hot plate, then heat-treated at 80 °C for 24 h in a drying oven and washed with water at 80 °C to remove CTAB. Finally they were dried again at 80 °C in the drying oven.

2.3. Characterization

Contact angles of films were measured using a KRUSS DSA 100 contact angle analyzer. CTAB specific peaks were investigated using a Thermo Scientific IR 200 Fourier Transform Infrared Spectroscopy (FT-IR) spectrometer, in the attenuated total reflection (ATR) mode with ZnSe crystal in contact with a sample.

Atomic force microscope (AFM) images of porous structures in films were obtained with a Nanoscope III scanning probe microscope controller, from Multimode AFM of Digital Instrument, in the tapping mode. Tapping tips used in the measurement were 4 μm thick, 125 μm long, 30 μm wide; they had a resonance frequency of 320 kHz and a force constant of 42 N/m. Adhesion of AR films was measured using the P-A-T Paint Adhesion Test Kit of Paul N. Gardner Company, Inc. An 11 tooth 1.0 mm cutter and a tape LA-26 (thickness: 1.5 μm, steel adhesion: 2.59 N/cm^2) were used. Reflectivity was measured using a Varian Cary 5000 UV-Vis-NIR spectrophotometer and a Scinco S-3100 UV-Vis Spectrophotometer. Nitrogen-gas physisorption measurements were conducted at 77 K using a Micromeritics ASAP 2010 apparatus. From the saturation adsorption volume of nitrogen-gas, the porosity P was calculated by the following relation (skeleton specific volume of SiO_2 was assumed to 0.37 cm^{3}g^{-1}) [12],

$$P = V_p / \left(V_p + 0.37\right) \tag{2}$$

$$V_p = 1.547 \times 10^{-3} V_d \tag{3}$$

where V_p is the volume of the liquidated nitrogen corresponding to the total pore volume, and V_d is the saturation adsorption volume at standard temperature and pressure (STP).

3. Results and discussion

3.1. Contact angle analysis

From Fig. 1a, glass substrates had a water contact angle $\Phi = 66°$, and were therefore hydrophilic. In contrast, PET substrates had $\Phi = 114°$, and so were relatively hydrophobic surface from Fig. 1b. If a substrate surface is hydrophilic, films can be easily deposited on them by sol–gel coating owing to their good wettability. However, if the surface is hydrophobic, coating solutions on it may be difficult. To identify whether the silica solutions can be coated on PET substrates, contact angles were measured. As shown in Fig. 1c, the solutions had

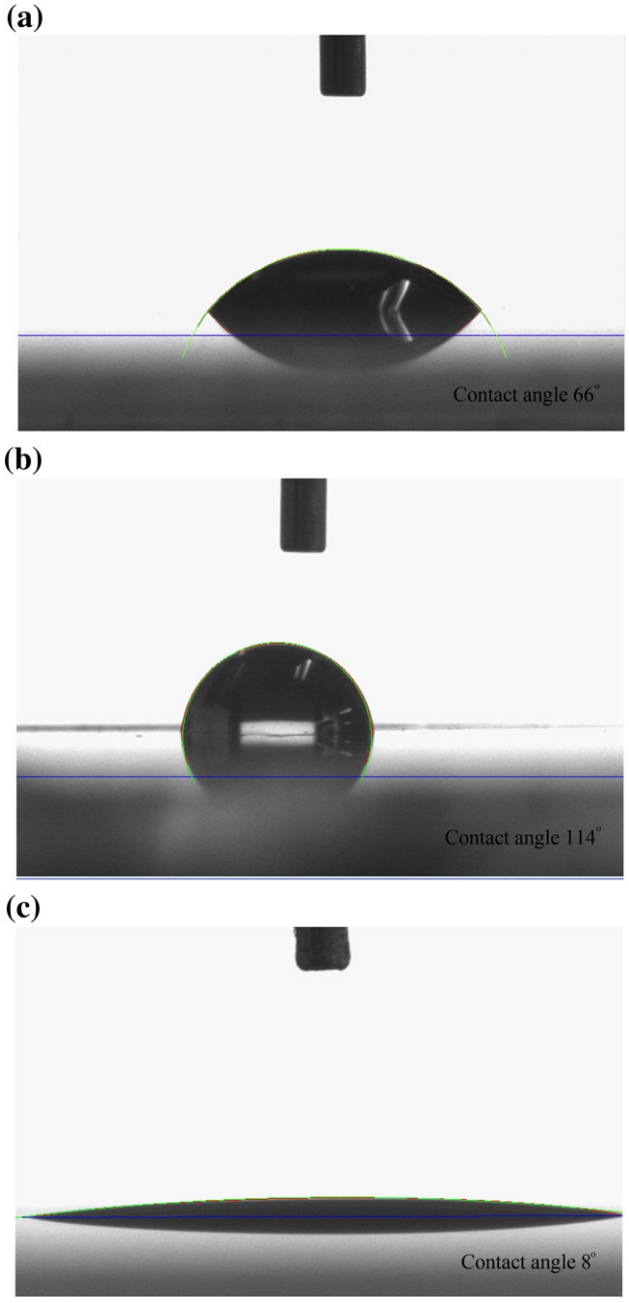

Fig. 1. Contact angle (a) of water on glass, (b) of water on PET, (c) of silica sol on PET.

$\Phi \approx 8°$, therefore they were relatively hydrophilic, which suggests that they can be easily spin-coated on PET substrates.

3.2. FT-IR analysis

To fabricate single-layered AR coatings, thin films having $n_1 = 1.26$ should be deposited on the PET substrates, which have $n_s = 1.59$. Eq. (4) determines n_1 of AR films [13].

$$n_p^2 = \left(n^2 - 1\right)(1 - P) + 1 \tag{4}$$

where n_p is the refractive index of the porous material, and n is that of a nonporous one, and P is the porosity.

Thin films having a specific index of refraction can be prepared by giving them a certain porosity. Micelle structures were created by employing a structuring agent, CTAB, which was then removed by