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Fabrication and characterization of silica anti-reflective films with phosphoric acid template

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ABSTRACT

In this work, the feasibility is investigated and confirmed that H_3PO_4 is used as pore-forming agent in silica antireflective film. The films are prepared by sol–gel method and spinning-coating technique and studied by field-emission scanning electron microscopy (FE-SEM), visible spectroscopy and ellipsometer. The impact of H_3PO_4 concentration on transmittance is also examined. Transmittance spectra show that silica films feature a marked increase of substrate transmittance almost at all measured wavelengths (325–1000 nm) owing to the addition of H_3PO_4. With the decrease of H_3PO_4 concentration, films transmittance will rise first and then decrease slightly. And with an increase of 4.1%, a maximum light transmittance of 95.01% is obtained, which is comparable to some other antireflective films using organic templates.

1. Introduction

Antireflective (AR) films have been widely utilized in various fields, such as panel glass, solar collectors, high-power lasers and so forth [1–4]. Among them, the applications in solar power field and display devices have become the important markets [5]. Therefore, it's worthwhile to develop high-performance and cost-effective AR films.

Many methods have been employed to fabricate AR films, such as chemical etching [6], chemical vapor deposition (CVD) [7] and sol–gel process [8]. Among them, sol–gel process attracts great attention owing to many advantages like high process speed, low cost and, especially, its capability of precisely controlling the microstructure of deposited films [9,10].

In order to elevate transmittance, AR films have to meet several requirements, including homogeneous pore distribution, pore size dramatically smaller than the wavelength of light (i.e. mesoporosity: 2–50 nm) and nanometric particle size [8]. Among the methods to fulfill these requirements, adding removable template agent is an effective one. The commonly-used agents include Pluronic F127 [4] and CTAB [11], etc. Although these agents can improve transmittance, all of them are organics and, hitherto, few inorganic agents are reported yet. In this work, we demonstrate the feasibility that inorganics, H_3PO_4, acts as a pore-forming agent in AR films for the first time and also examine the impact of H_3PO_4 concentration on transmittance.

2. Experimental procedure

Materials: Tetraethyl orthosilicate (TEOS, Sinopharm), phosphoric acid (H_3PO_4, 85% aqueous solution, Sinopharm), hydrochloric acid (HCl, 36–38% aqueous solution, Sinopharm) and absolute ethanol (EtOH, Sinopharm) were used as-received without further purification.

Preparation of films:

1. The silica sol was prepared by stirring the mixture of TEOS, deionized water and hydrochloric acid at a molar ratio of 1:3:0.004 (TEOS:H_2O:HCl) under ice-water condition until it became transparent and homogeneous.
2. Sols used for depositing films were prepared as follows. H_3PO_4 and EtOH were mixed and stirred first at the molar ratio of 1:22, 1:66, and 1:110 (H_3PO_4:EtOH), respectively for 10 min, where EtOH was used as dilute to adjust H_3PO_4 concentration. Later, the silica sol obtained in step 1 was added to these mixtures in a molar ratio of 4:6 (H_3PO_4:TEOS), respectively. The mixtures thus obtained were then stirred under ice-water condition for 1 h and used as sols for depositing films and named as A-22, A-66 and A-110.
3. Films were deposited on to one surface of the cleaned glass substrates, which were 1.2 mm-thick and in size of 25 mm × 25 mm, by spin-coating method at the speed of 3000 r min^{-1} for 1 min using the sols obtained in step 2. These films were named as A-22, A-66 and A-110, correspondingly.
4. Films obtained were heat-treated in the programmable muffle furnace at the rate of around 1 °C min^{-1} to 400 °C and held at

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that temperature for 2 h. After that, these films were immersed in boiling deionized water for 40 min and then dried at 200 °C for 2 h. The schematic illustration of the preparation procedure is shown in Fig. 1.

Characterization: Total transmittance spectra of films were measured at room temperature by a visible spectrophotometer (723PC, Shanghai Precision Instrument Co, Ltd, China) in the wavelength range of 325–1000 nm. The top-view and cross-section images of films were examined by field emission scanning electrons microscope (FE-SEM) (Hitachi S-4800, Japan). The reflective indexes of films were determined by ellipsometer (W-Vase, J.A. Woollam Co. USA).

3. Results and discussion

Morphology of SiO_2 AR films: Fig. 2 shows the top-view and cross-sectional images of A-22, A-66 and A-110. The top-view images evidently show that A-22 to A-110 have distinguishing pores more or less, indicating that H_3PO_4 indeed functions as a pore-forming agent, which is consistent with the previous studies [12,13]. Regarding the pore-forming mechanism of H_3PO_4, one explanation is that hydrogen bonds may form between H_3PO_4 molecules and silanol groups on the surface of the pore walls and H_3PO_4 aggregates along the pore walls and retains in film during gelation, which results in the formation of pore channels with different widths [13]. The aggregation of H_3PO_4 will increase with the increase of H_3PO_4 content or concentration, which in turn increases pore size and volume. The comparison of the top-view images of A-22 to A-110 in Fig. 2 shows pore size and porosity may reduce with the decrease in H_3PO_4 concentration. Besides, from the cross-section images of A-22, A-66 and A-110 shown in Fig. 2, we can see the thickness of each film is ~220 nm, ~100 nm and ~55 nm, respectively, indicating that film thickness will decrease with the increase of EtOH.

Transmittance of films: In order to investigate the transmittance of films, a visible spectra study was performed. As shown in Fig. 3, it's obvious that the overall transmittance curves rise first and then fall with the decrease of H_3PO_4 concentration. The transmittance curve of A-66 is the highest almost at all measured wavelength. Why A-66 possesses the best transmitting performance can be explained from the perspective of pore size, reflective indexes and thickness of films. Specifically, in order to achieve zero reflection in an air medium, the relationship among the reflective indexes of the air medium (n_m=1), glass substrate (n_s) and AR film (n_f) must be [14]

$$n_f = \sqrt{n_m n_s} \tag{1}$$

And the thickness of film, T, must also meet thickness requirement:

$$T = \frac{m\lambda}{4n_f} \tag{2}$$

where m is the odd number 1, 3, 5 etc., λ is the wavelength of the incident beam and n_f is the refractive index of film [14,15].

In this study, the reflective index of substrate, n_s, is 1.52. From Eq. (1), it can be calculated that, for the minimum reflectivity to be zero, n_f must be 1.23. The refractive index ranges of A-22, A-66 and A-110 in the measured wavelength range, which were examined by ellipsometer, are 1.2019–1.2781, 1.3001–1.3138 and 1.3137–1.348, respectively. From the sub-section 'Morphology of SiO_2 AR films', we know the thickness of A-22 to A-110 is ~220 nm, ~100 nm and ~55 nm. Based on these data, it's reasonable to expect that A-22 may show a good transmitting performance in the whole measured wavelength, especially, in the wavelength range of 353–375 nm, which is calculated from Eq. (2) when m is 3. However, as shown in Fig. 3, its performance is the worst and even lower than that of glass substrate, which may be owing to the over-size pores in A-22. Specifically, when small amount of EtOH is added to sol, H_3PO_4 concentration is so high that the aggregation of H_3PO_4 increases in sol, finally resulting in the formation

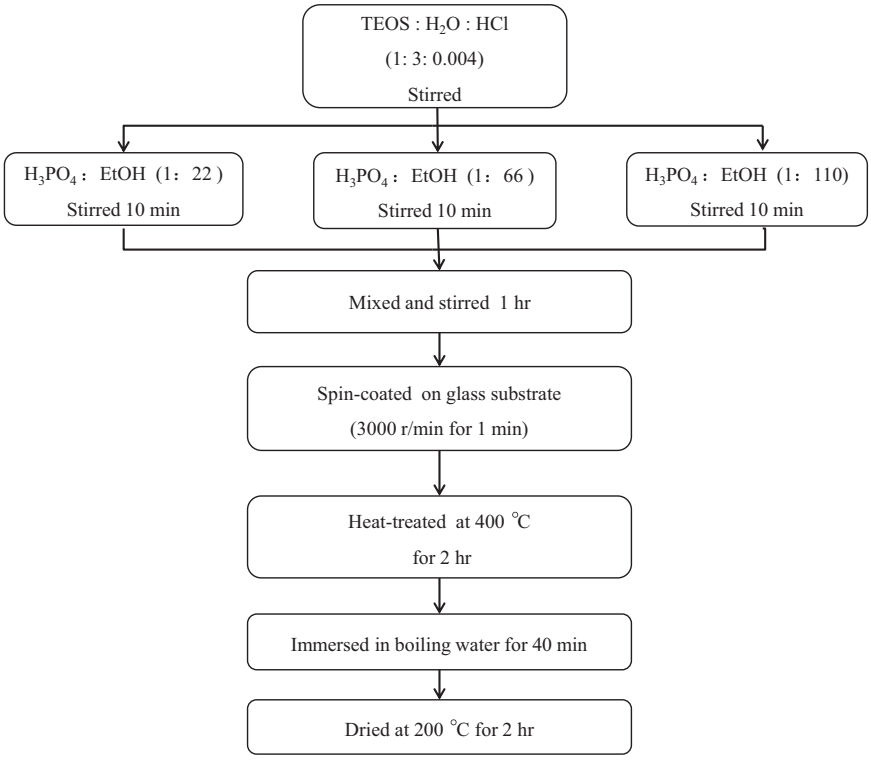

Fig. 1. The flow chart of the preparation of SiO_2 antireflective films.