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Self-cleaning and antireflection properties of titanium oxide film by liquid phase deposition

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ABSTRACT

In this investigation, titanium oxide films were deposited on silicon substrate by liquid phase deposition using a deposition solution of ammonium hexafluoro-titanate and boric acid. The concentration of the boric acid in the deposition solution controls the rate of deposition of titanium oxide film. The titanium oxide film becomes superhydrophilic with a contact angle around 4° after irradiation by UV light. The average reflectance is 5.3% at wavelengths from 400 to 800 nm. Superior wetting and antireflection properties make the film suitable for use in silicon-based solar cells.

1. Introduction

Antireflective coatings (ARC) are required to reduce the optical loss of many optical devices, such as optical lenses, flat panel displays and solar cells [1,2]. Reflection occurs at the interface where the refractive index changes abruptly. Several transparent materials have already been used as ARCs. These include SiO_2 ($n = 1.44$), Si_3N_4 ($n = 1.9$), TiO_2 ($n = 2.3$), Al_2O_3 ($n = 1.86$), Ta_2O_5 ($n = 2.26$) and SiO_2–TiO_2 ($n = 1.8$–1.96) [3–8]. Among these ARC films, the TiO_2 film has attracted much attention owing to its self-cleaning and antireflection properties [9,10]. The self-cleaning property of TiO_2 film follows from two unique photo-induced phenomena: photocatalysis and photo-induced superhydrophilicity. Therefore, organic pollutant that is adsorbed on the surface of a TiO_2 film can be decomposed under illumination by ultraviolet (UV) light. Then the contaminant can be washed off by rainwater because of its photo-induced superhydrophilicity.

Antireflective coatings are generally formed by vacuum processes, such as evaporation [11], sputtering [12], and plasma-enhanced chemical vapor deposition (PECVD) [13]. All of these methods can produce films with uniform thickness and favorable optical properties. However, conventional vacuum deposition processes are expensive and unsuitable for continuous mass production, especially for forming coatings for use in low-cost solar cell. Recently used non-vacuum processes for depositing an ARC film on a substrate include sol–gel dip coating, spin coating, spray pyrolysis and liquid phase deposition (LPD). The LPD method is used herein to fabricate ARC films to ensure low cost, uniformity, favorable adhesion, mass producibility, and the formation of large-area optical films.

Liquid phase deposition is a low-temperature (including room temperature) growth process that has other advantages such as high selectivity, large area, simplicity, ease of change of the film composition, and support of mass production [14,15]. According to previous investigation, a $Ti_xSi_{1-x}O_y$ film can be deposited on an Si substrate by the LPD method with a hexafluorotitanic acid (H_2TiF_6) source at low temperature [16]. Therefore, the refractive index of the LPD-TiO_2 film is lower than those of films formed by other deposition methods and such a film can be utilized in silicon solar cells. In this investigation, ammonium hexafluorotitanate ($(NH_4)_2TiF_6$) and boric acid (H_3BO_3) were used as the starting materials in titanium oxide deposition. The self-cleaning and antireflective properties of LPD-TiO_2 films on Si substrate were studied.

2. Experiment

2.1. LPD-TiO_2 films deposition

A p-type Si (100) wafer was utilized as the substrate, and its resistivity was 10–20 Ω·cm. Silicon substrate was degreased in solvent and then chemically etched in a solution ($HF/H_2O = 1{:}10$) for 30 s and then rinsed in deionized water. The deposition system contains (1) a temperature-controlled water bath that provides a uniform deposition temperature with an accuracy of ±0.1 °C and (2) a Teflon vessel, which contains the deposition solution. A 20 ml volume of $(NH_4)_2TiF_6$ (0.2 M) solution that was saturated with TiO_2 powder was mixed with 20 ml H_3BO_3 (0.4–0.8 M) for depositing TiO_2 films. The deposition temperature was maintained at 60 °C during the deposition. Following deposition, the silicon wafer was rinsed in deionized water and dried with purified nitrogen gas. Finally, the samples were annealed at 700 °C in air for 1 h to convert the amorphous phase to the crystalline anatase structure.

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The thickness and refractive index of the LPD-TiO_2 were measured by ellipsometry. X-ray diffraction (XRD) measurements were made to examine the constituent phases of TiO_2 films. Field emission scanning electron microscopy (FE-SEM) was utilized to determine thickness and morphology. The depth profile of the LPD-TiO_2 film was analyzed by X-ray photoelectron spectroscopy (XPS). The water contact angles were measured at room temperature using a contact angle meter by the sessile drop method. The reflection spectra of the samples at wavelengths from 400 to 800 nm were obtained using an UV–VIS-NIR spectrophotometer.

2.2. Photocatalysis studies

The photocatalytic activities of the prepared LPD-TiO_2/Si samples were evaluated using methylene blue (MB). A series of 0.01 mmol/L methylene blue solutions were prepared. The LPD-TiO_2/Si samples had dimension of 2×2 cm^2. Then the sample was placed in Petri dishes, to which was added 30 ml MB solution. The reaction was illuminated under a 20 W UV lamp (FL20S-BLB, wavelength = 310–400 nm) in a black box. The light intensity was measured using a light intensity meter from Photon Technology International and controlled at 1 mW/cm^2 throughout this investigation.

Photocatalytic reactions that occur on the surface of a photocatalyst can be expressed using the Langmuir–Hinshelwood model [17]. The photo-decolorization reaction rate after adsorption equilibrium is given by

$$R(t) = [1-(\mathrm{abs}(t)/\mathrm{abs}(t_0))]100[\%] \quad (1)$$

where abs(t) and abs(t_0) are the degrees of adsorption of MB solutions at time = t and $t = 0$, respectively, at $\lambda_{max} = 650$ nm, and $R(t)$ is the apparent photo-decolorization reaction rate.

3. Results and discussion

Fig. 1 plots the deposition rate of LPD-TiO_2 film on Si substrate as a function of H_3BO_3 concentration. The deposition rate increases with H_3BO_3 concentration and reaches a maximum at 0.7 M. The deposition rate is linearly related to concentration in the range 0.4–0.7 M. The deposition rate falls dramatically as the concentration of H_3BO_3 rises above 0.7 M, owing to the precipitation of TiO_2 in the deposition solution. Fig. 2 shows the refractive index and extinction coefficient of as-deposited and annealed LPD-TiO_2 film on Si substrate for various H_3BO_3 concentrations. The refractive index of as-deposited LPD-TiO_2 film increases slightly from 1.72 to 1.81 with the H_3BO_3 concentration. Following the annealing treatment, the trend of refractive index is similar to the as-deposited sample, which increases slightly from 1.73 to 1.82 with the H_3BO_3 concentration. The refractive index of LPD-TiO_2 film is lower than that by other methods [18], because the $Ti\_Si_{1-x}O_y$ transition layer may be present in the LPD-TiO_2/Si interface. Since the refractive indices of SiO_2 and TiO_2 are 1.4 and 2.4, respectively, the refractive index of $Ti\_Si_{1-x}O_y$ films can be controlled by varying the Si content. Hence, the refractive index can be tuned by adjusting the thickness or Si content of the $Ti\_Si_{1-x}O_y$ film. The controllability of the refractive index and film thickness enables an antireflection coating layer to be applied to LPD-TiO_2 films for Si-based solar cells. The extinction coefficient of as-deposited and annealed LPD-TiO_2 film decreases slightly with the H_3BO_3 concentration, which implies the smaller absorption and transparent with less optical energy loss in the deposition condition of higher H_3BO_3 concentration.

Fig. 3 shows an FE-SEM cross-sectional image of the LPD-TiO_2/Si structure with an H_3BO_3 concentration of 0.5 M. The thickness of the LPD-TiO_2 film is approximately 80 nm. Fig. 4 presents the XPS depth profile of LPD-TiO_2 film on a Si substrate. It shows a transition layer of $Ti\_Si_{1-x}O_y$ with a thickness of approximately 48 nm at the LPD-TiO_2/Si interface. The high concentration of Si in the transition layer arises from the etching of the Si substrate by HF from the reaction of deposition solution. The equilibrium for the formation of HF in the deposition solution and the reaction of Si with HF are as follows [19]

$$[TiF_6]^{2-} + 6H_2O \leftrightarrow [Ti(OH)_6]^{2-} + 6HF \quad (2)$$

$$Si + 6HF \leftrightarrow H_2SiF_6 + 2H_2 \quad (3)$$

The equilibrium reactions for $Ti\_Si_{1-x}O_y$ are as follows.

$$[Ti(OH)_6]^{2-} + 2\,H^+ \leftrightarrow TiO_2 + 4H_2O \quad (4)$$

$$H_2SiF_6 + 2H_2O \leftrightarrow SiO_2 + 6HF \quad (5)$$

$$H_3BO_3 + 4HF \leftrightarrow BF_4^{\ -} + H_3O^+ + 2H_2O \quad (6)$$

H_2SiF_6 is formed close to the surface of the substrate. During the initial growth, TiO_2 and SiO_2 are nucleated on the substrate surface to form $Ti\_Si_{1-x}O_y$. The H_2SiF_6 source decreases as the coverage of deposited the $Ti\_Si_{1-x}O_y$ film increases. The film transforms gradually into TiO_2 with the thickness of the LPD-ARC film increases. The reaction proceeds with the incorporation of H_3BO_3, which consumes F ions with the formation of stable BF_4^- ions, consistent with Eq. (6) and shift the equilibrium from the left side to the right side of Eqs. (2) and (4). Then, the proportion of HF in the deposition solution decreases and the silicon substrate becomes slightly etched, causing

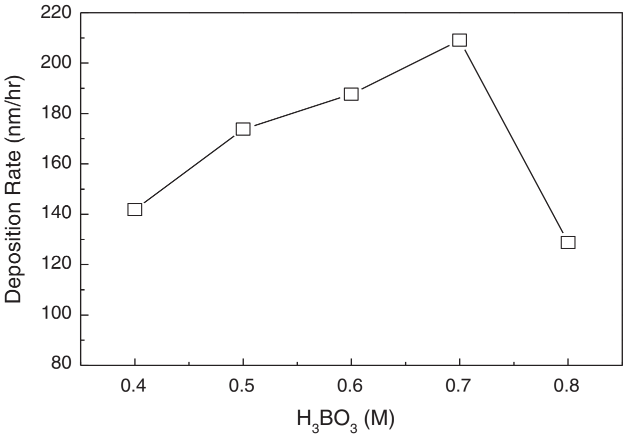

Fig. 1. Deposition rate of LPD-TiO_2 as a function of H_3BO_3 concentration.

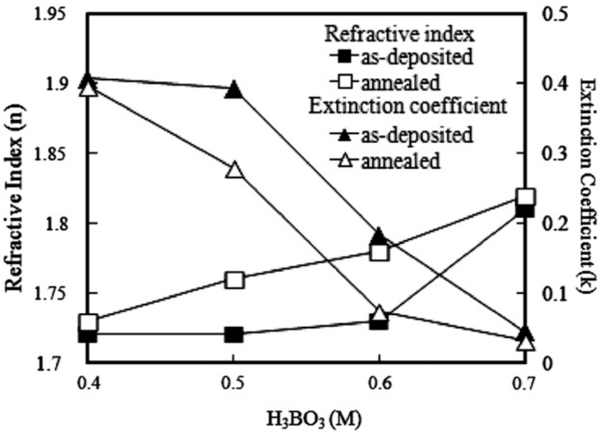

Fig. 2. Refractive index and extinction coefficient of LPD-TiO_2 film on Si substrate for various of H_3BO_3 concentrations.