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Thin Solid Films 499 (2006) 83 – 89

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Fabrication and characterization of TiO_2 thin film prepared by a layer-by-layer self-assembly method

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Available online 16 August 2005

Abstract

Titanium dioxide (TiO_2) thin films assembled with TiO_2 nanoparticles and oppositely charged polyelectrolytes or titanium (IV) bis(ammonium lactato) dihydroxide (TALH) were successfully fabricated via a layer-by-layer (LBL) self-assembly method at room temperature. Especially, by using the quartz crystal microbalance (QCM) to monitor the in-situ deposition phenomenon of TALH that is saturated and then separated from the film before and after the deposition of 30 s at low pH, the anatase TiO_2 multilayer films fabricated with 30 s deposition in TALH adjusted to pH 2.5 showed a higher refractive index (ca. $n = 1.75$), a denser film growth, and a lower surface roughness (ca. 10.5 nm) than those of the films deposited in different conditions. This film showed a high transmittance in visible range for optical applications and photocatalytic properties by decomposing methyl orange molecules gradually according to UV irradiation time. In addition, as the pH of TALH was decreased from pH 5.5 to 2.0, the thickness of $(TiO_2/TALH)_{30}$ film was increased from ca. 85 nm to ca. 442 nm.

Keywords: Layer-by-layer self-assembly method; TiO_2 thin film; Polyelectrolyte; Quartz crystal microbalance

1. Introduction

In the past several years, there has been increasing interest in the fabrication of TiO_2 thin films because they present useful optical, electrical, and chemical properties such as high refractive index [1], high relative dielectric constant [2], remarkable solar energy conversion [3,4], and photocatalysis [5]. Therefore TiO_2 thin film can be a promising material for an optical filter [6], antireflection film [7], a self-cleaning coating [8], a high efficient dielectric [9], and a solar cell [10].

TiO_2 thin film has been fabricated by several methods such as a sol–gel synthesis [11], sputtering [12] and chemical vapor deposition (CVD) [13]. However, these processes that require a high temperature, a high qualitative vacuum system and intricate equipments have a limit of film area or thickness, mechanical instability, and high cost. However layer-by-layer (LBL) self assembly method using sequential adsorptions of ionized polyelectrolytes and oppositely charged materials in aqueous solutions has lots of advantages such as a simple process, low temperature deposition, no limit of thickness and needless of complicated equipments [14,15]. In addition, the thickness of thin film can be controlled with a nanoscale [16].

In previous reports, TiO_2 thin films composed of positively charged TiO_2 nanoparticles [17] and oppositely charged polyelectrolyte [18] or consisted of polyelectrolyte and negatively charged titanium (IV) bis(ammonium lactato) dihydroxide (TALH) [19] have been successfully fabricated by a LBL self-assembly method. However the refractive index of the film composed of TiO_2 nanoparticles and polyelectrolytes is significantly decreased because of the presence of pores and polyelectrolyte with low refractive index relatively [20]. On the other hand, although the TiO_2 thin film comprising polyelectrolyte and TALH solution which is stable and double negatively charged inorganic precursor [21] shows high refractive index ($n = 1.68 \sim 1.8$), this film has a small film growth with the average thickness (ca.1.5 $\sim$ 5 nm) of a bilayer [22,23]. In addition, the film growth phenomenon between TALH and polyelectrolytes or

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doi:10.1016/j.tsf.2005.07.001

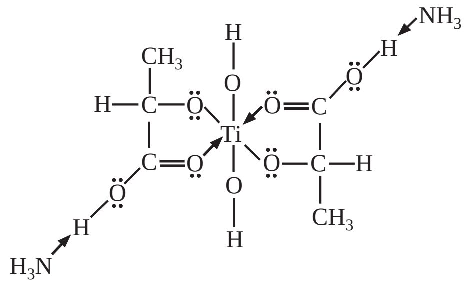

Fig. 1. Assumed molecular structure of the non-ionized form of TALH (the arrows indicated electron pairs).

nanoparticles has not been sufficiently explored as functions of the immersion time or the pH of solution [19].

Quartz crystal microbalance (QCM) has been used for the monitoring of the in-situ deposition phenomenon of materials on substrate in LBL assembly process [24] as well as a gas sensor [25,26], because when material is deposited on the electrode of QCM, frequency is decreased in proportional to the mass change by the Sauerbrey relation [27]:

$$df = -\frac{f^2}{N\rho A}dm \quad (1)$$

In this study, we report that TiO_2 thin films assembled with TALH and TiO_2 nanoparticles have been successfully fabricated with a low surface roughness, high refractive index, improved thickness growth and a high transmittance by monitoring the deposition phenomenon depended on the pH of solution as well as immersion time into TALH using a QCM. In addition, the properties of these films were compared with that of films comprising TiO_2 nanoparticles and polyelectrolyte.

2. Experimental details

2.1. Materials

The used starting materials were oppositely charged poly(dimethyldiammonium chloride) (PDDA, 20 wt.%, Aldrich) and TiO_2 colloidal solution (ca. 7 nm in primary particle size, anatase) obtained from Ishihara Sangyo, Ltd. (Japan). Poly(phosphoric acid) (PPA, Wako) and poly(sodium 4-styrenesulfonate) (PSS, Mw = 70,000, Aldrich) were used as a negatively charged polyelectrolyte. Titanium (IV) bis(ammonium lactato) dihydroxide (TALH, 50 wt.%, Aldrich) with double negative charges [21] was selected as an inorganic precursor. The molecular structure of TALH is shown in Fig. 1. The concentration of PPA and PDDA were adjusted to 0.01 M using ultra pure water (>18 MΩ cm) and then the pH of solutions was adjusted with NaOH or HCl. 0.1 wt.% of TiO_2 colloidal solution was adjusted to pH 2.5 and the pH of TALH solution was adjusted from 5.5 to 2.0 with HNO_3. Glass, Si/SiO_2, and QCM (AT-cut, 10 MHz) with a gold electrode were used as substrates.

2.2. Preparation of thin films

Negatively charged substrates, glass and Si/SiO_2, were obtained by KOH (1 wt.%) treatment in ultrasonication for 5 min and then rinsed in ultra pure water (pH 5.5~6.5). QCM was also carried out KOH treatment and then the 3 bilayers of (PDDA/PSS) were assembled on electrode to diminish the surface influence of each QCM.

Substrates and QCM were immersed into TiO_2 colloidal solution and polyelectrolytes for 10 min and TALH solution for 10 s ~ 10 min. Fig. 2 depicts the schematic illustration of the procedures to fabricate the (TiO_2/TALH) multilayer thin film. Rinse procedures (1 min × 3 times) were subsequently carried out after immersion into solutions using ultra pure water. These coating procedures were repeated 30 times. When we deposit material B over A with 30 times, we describe as $(A/B)_{30}$.

2.3. Characterization of multilayer thin films

The surface microstructure and the cross-section of thin film deposited on glass substrate were investigated by a field emission scanning electron microscope (FE-SEM, Hitachi S-4700) and the root mean squared (RMS) surface roughness was measured by an atomic force microscope (AFM, Digital Instrument nanoscope βa) in a tapping mode. The RMS roughness was calculated according to the following Eq. (2):

$$RMS = \sqrt{\frac{\sum(Z_i - Z_{ave})^2}{N}} \quad (2)$$

where Z_i is the height on the Z-axis of feature i, Z_{ave} is the average height of the entire image, and N is the number of points in image.

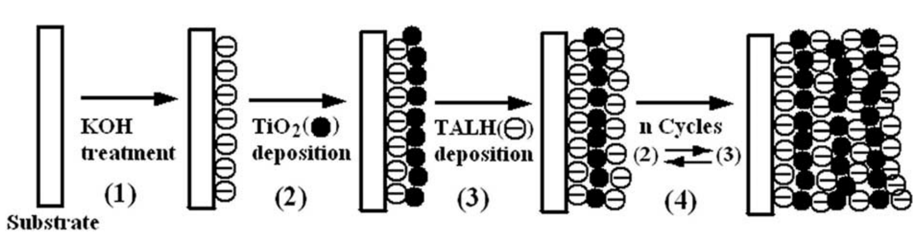

Fig. 2. Schematic illustration of the procedures to fabricate the multilayer thin film consisted of (TiO_2/TALH).