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Investigation on ultrathin titanium oxide films synthesized by surface sol–gel method

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ABSTRACT

Ultrathin titanium oxide films were synthesized on glass substrates by surface sol–gel method. The films were grown by sequential immersion in $TiCl_4$ solution and water. The film morphology, structure and property were characterized by atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV–visible spectroscopy. The results indicate that the films grow at a rate of about 2–3 nm per cycle and present an island-like growth mode. The film show an amorphous state and not a strict equilibrium TiO_2 structure. Furthermore, the film absorbance gradually increases with the depositing cycle.

1. Introduction

Functional oxide films have been widely used as semiconductors, dielectrics, electrodes, catalysts, sensors, and so on. However, with the miniaturization development of electronic and optoelectronic devices, the thickness of using materials is required to decrease to the nanometer level [1]. Therefore, it is especially important of preparing the ultrathin oxide films with nanometer precision. Various chemical vapor deposition and physical techniques are often used to fabricate the ultrathin films, but their equipment cost and technological demand are high. Comparatively, the wet chemical synthesis represents a simple and inexpensive technique for fabricating films. Nevertheless, the obtained films are easy to be cracked and peeled off due to the solvent evaporation, especially for the ultrathin films [2–4]. Hence, the currently primary problem is to find a technically simple and economical method for preparing the ultrathin oxide films.

Surface sol–gel (SSG) method is a newly advanced technique for fabricating ultrathin films [5–7]. SSG is a wet chemical synthesis technique, which can achieve the precise control of film thickness and obtain some especial properties by adjusting the particle size. Compared with conventional deposition methods, this process does not require high temperature or expensive vacuum equipment, and also has the compatibility with substrate surface [2,3]. Up to now, SSG method has been successfully applied to the synthesis of some ultrathin oxide films [5–12]. In this work, the ultrathin titanium oxide films were synthesized by SSG technique and characterized by atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV–visible spectroscopy.

2. Experimental

The substrates used in this experiment were glass plates. First, the glass substrates were degreased with acetone and ethanol for 10 min respectively. After that, the substrates were ultrasonically washed in distilled water for 30 min and dried in clean air. The above steps could favor the growth of titanium oxide films. Next, the substrates were placed in a solution of $TiCl_4$ in acetone (100 mM) for 1 min. The substrates were then rised with acetone and dried in in air at room temperature. Finally, the substrates were hydrolyzed in distilled wateranddried in air at 60 °C. Here, the above process was recorded as one depositing cycle. By repeating this process, multilayer films could be synthesized.

The surface morphologies of titanium oxide films were examined in Nanoscope III a-type atomic force microscope (AFM). AFM measurements were performed in tapping mode. The phase structure was characterized by Philips X-pert X-ray diffraction (XRD), using a Cu Ka radiation source (0.15418 nm). The surface chemical state was analyzed with PH15700 X-ray photoelectron spectroscopy (XPS), using a Mg *Ka* source (1253.6 eV). The incident angle of X-ray beam was 30° with respect to the sample surface.

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All binding energies were calibrated with the C 1s peak at 284.5 eV. The optical property was measured using Perkin-Elmer Lambda 9 UV–visible–NIR spectrophotometer.

3. Results and discussion

3.1. Surface morphology

AFM images of glass substrate and titanium oxide films with different depositing cycles are shown in Fig. 1. Before deposition, the glass substrate presents a relatively even surface (Fig. 1(a)). After depositing titanium oxide films, the surface morphologies can be described as the closed-packed particle islands with a special cluster feature. At the beginning of depositing, the particle islands unevenly and loosely distribute on the film surface (Fig. 1(b)). With the increase of deposition cycles, the particle islands gradually become even and dense and the island size tends to be uniform. On the film surfaces with 5 and 10 cycles (Fig. 1(c) and (d)), the particle islands cover the entire surface, but the boundaries are very distinct among the islands. As the depositing cycles increase, the particle islands continuously aggregate and the island boundaries are not very clear, and thus the surface roughness becomes smaller and smaller (Fig. 1(e)). When depositing for 40 cycles (Fig. 1(f)), the film tends to be planar, further implying the islands aggregated together. The above results indicate that the titanium oxide films deposit on the substrates in a particle island mode. With the increase of depositing cycles, the islands' size and distribution become uniform and the particle islands tend to be aggregated together. This growing mode is similar to that of the silica films prepared by the same method [13].

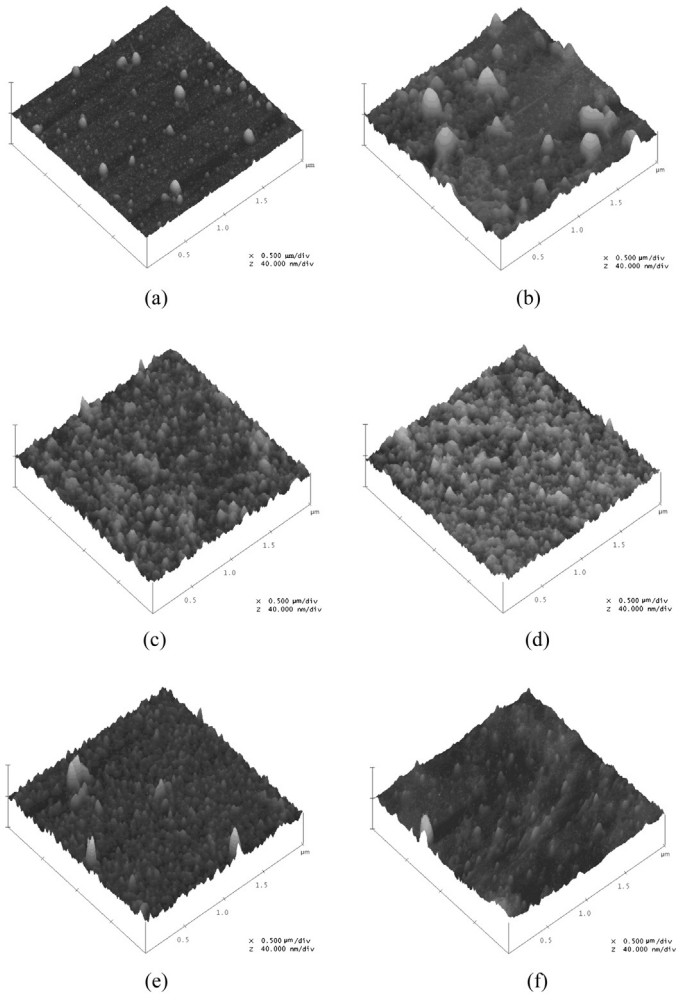

Fig. 1. AFM images of substrate and titanium oxide films with different depositing cycles. (a) glass substrate, (b) 3 cycles, (c) 5 cycles, (d) 10 cycles, (e) 20 cycles, (f) 40 cycles.

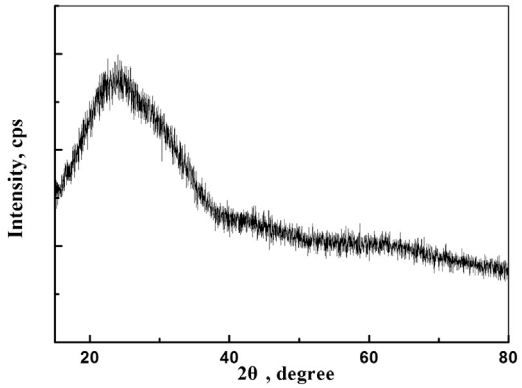

Fig. 2. XRD patters of titanium oxide film with 40 cycles.

3.2. XRD analysis

XRD measurements were performed to further analyze the film structure. The corresponding result is presented in Fig. 2. After depositing titanium oxide film, the sample shows a peak shape similar to that of the substrate. There is one broaden peak at 2θ of 24°, which is the typical diffraction peak of amorphous SiO_2 from the substrate [14,15]. Except that, no obvious diffraction peak can be observed in Fig. 2. This result suggests that the as-deposited titanium oxide films are amorphous, which is because that the as-deposited films have not been heat-treated.

3.3. XPS analysis

In order to analyze the chemical state of as-deposited titanium oxide films, XPS measurements were carried out. Fig. 3 gives the XPS full spectrum of titanium oxide film with 40 cycles. The binding energies at 285.9 eV, 458.4 eV and 530.1 eV correspond to the C 1s, Ti 2p and O 1s peaks respectively. The C 1s peak is derived from the absorbent carbon on the sample surface. Except the three peaks, the other peaks in Fig. 3 all come from the glass substrate.

The XPS spectra of Ti 2p and O 1s core levels of titanium oxide film with 40 cycles are shown in Fig. 4. Due to the electron spin-orbit coupling, Ti 2p splits into two energy levels. One at 458.2 eV is assigned to Ti 2p3/2 peak and the other one at 463.8 eV is

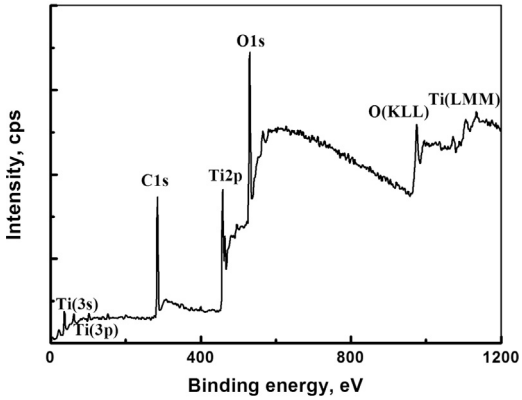

Fig. 3. XPS full spectrum of titanium oxide film with 40 cycles.