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Effects of Thermal Annealing and Film Thickness on the Structural and Morphological Properties of Titanium Dioxide Films

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Titanium dioxide (TiO_2) thin films having different thicknesses of 220, 260, and 300 nm were deposited onto well-cleaned *n*-type silicon substrates by reactive DC magnetron sputtering and annealed in the range of 200–1000 °C in steps of 200 °C. The effects of thermal annealing and thickness variation on the crystalline quality and surface morphology of the films were investigated by X-ray diffraction and atomic force microscopy measurements. It was found that the film quality and morphology depend on the annealing temperature. TiO_2 films exhibit a grain-like surface morphology. The root-mean-square roughness and grain size on the surface increase as a result of increasing film thickness.

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1. Introduction

Titanium dioxide (TiO_2) is one of the most studied metal oxides because of its applications such as photocatalysts [1–4], gas sensors [5, 6], solar cells [7, 8]. As is known, TiO_2 exists in amorphous form and in three different crystalline phases: rutile, anatase, and brookite [9]. Many of these applications depend on the structural and optical properties of TiO_2 [4]. Post-deposition thermal annealing has an important influence on the properties of TiO_2 films [9]. The purpose of this study is to determine the effects of thermal annealing and film thickness on the structural and morphological properties of TiO_2 thin films deposited by using a reactive DC magnetron sputtering technique.

2. Experimental details

The TiO_2 thin films having thicknesses of 220, 260, and 300 nm were deposited on *n*-type silicon (1 0 0) substrates by reactive DC magnetron sputtering. After deposition, the films were thermally treated in air for 2 h at 200, 400, 600, 800 and 1000 °C. Surface morphology and crystallinity of the films were characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements. The AFM scans were carried out at 3 μm × 3 μm surface areas.

3. Results and discussion

Figure 1 illustrates XRD patterns of the as-deposited and annealed films. As is seen, the films deposited by a reactive DC magnetron sputtering have polycrystalline titanium oxide (TiO) structures. After annealing at 200, 400, and 600 °C, there appeared the A (0 0 4) and R (3 1 1) peaks in the anatase and rutile crystalline phases of TiO_2, respectively. However, at temperatures above 600 °C, the anatase peak disappeared and the rutile phase was dominant.

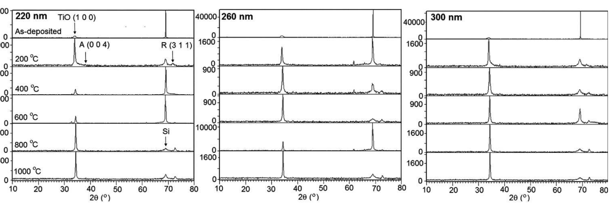

Fig. 1. XRD patterns of as-deposited and annealed films, which were identified as TiO (1 0 0) (JCPDS card no: 85-2084), TiO_2 A (0 0 4) (JCPDS card no: 89-4921), Si (4 0 0) (JCPDS card no: 80-0018), and TiO_2 R (3 1 1) (JCPDS card no: 89-4920).

Figure 2 shows AFM scans of the as-deposited TiO_2 films with different thickness. There appeared grains on the surfaces of the films. Similarly, Mathews et al. [4] observed the spherical features on the surface of a TiO_2 film deposited on glass substrates by sol–gel dip coating technique and reported that they evaporated away during annealing.

On the other hand, the sizes of the grains on the surfaces of the films increased with film thickness. Further-

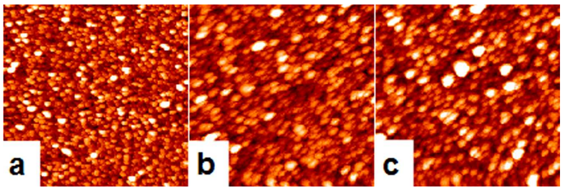

Fig. 2. AFM images of the as-deposited TiO_2 films having thicknesses of (a) 220, (b) 260, and (c) 300 nm. The surface RMS values of the films are 2.77, 3.13, and 3.42 nm for these scans of 3 μm $\times$ 3 μm, respectively.

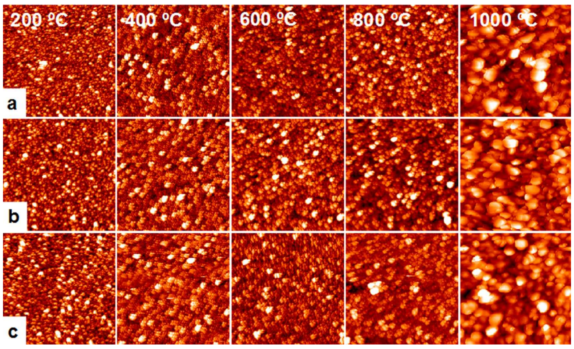

Fig. 3. AFM images of the annealed films having thicknesses of (a) 220, (b) 260, and (c) 300 nm. The scan area is 3 μm $\times$ 3 μm.

more, the root-mean-square (RMS) roughnesses on the surfaces of the films having thicknesses of 220, 260, and 300 nm were obtained as 2.77, 3.13, and 3.42 nm, respectively. From the RMS values, it can be seen that the film thickness increases the surface roughness, which is in agreement with the larger grains observed on the surfaces of thicker films.

Figure 3 shows AFM images of the TiO_2 films with different thicknesses annealed at 200, 400, 600, 800, and 1000 °C. After 200 °C annealing, no change was observed in the surface morphology of the films. However, the sizes of the grains decreased. The nanometer-size grains aggregated and a hillock-like structure on the surfaces of the films formed after 400 °C.

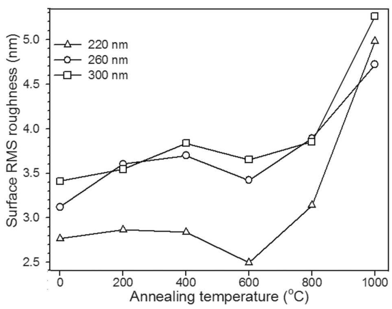

Fig. 4. The variation of the surface RMS roughness vs. the annealing temperature.

The surface RMS roughnesses of the films increased with increasing annealing temperature up to 400 °C, as shown in Fig. 4. After annealing at 600 and 800 °C, the surfaces of the films were covered by hillocks composed of agglomerated grains. The RMS roughness varied according to the densities and sizes of the hillocks and grains on the surfaces. In the case of annealing at 1000 °C, the films displayed hillocks with flat tops contrary to spherical grains or hillocks consisting of smaller grains observed at low temperatures, and higher RMS roughnesses. Furthermore, crystallite size of the films significantly increased as a result of completed coalescence process.

AFM observations clearly show that there is a remarkable change in surface morphology and roughness of the TiO_2 films depending on the annealing temperatures and film thicknesses. The most likely reason for the dramatic topographic change is the recrystallization in the films due to thermal annealing which is in agreement with that reported by Mathews et al. [4]. On the other hand, the larger grains or hillocks on the surfaces of the films reveal an improvement in the crystalline quality of the TiO_2 films, which is in agreement with XRD results.

Acknowledgments

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