



Effect of thermal annealing on the structure and microstructure of TiO₂ thin films

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Abstract : Nanostructured TiO₂ thin films have been prepared through chemical route using sol-gel and spin coating techniques. The deposited films were annealed in the temperature range 400–1000°C for 1 h. The structure and microstructure of the annealed films were characterized by GAXRD, micro-Raman spectroscopy and AFM. The as-deposited TiO₂ thin films are found to be amorphous. Micro-Raman and GAXRD results confirm the presence of the anatase phase and absence of the rutile phase for films annealed up to 700°C. The diffraction pattern of the film annealed at 800 to 1000°C contains peaks of both anatase and rutile reflections. The intensity of all peaks in micro-Raman and GAXRD patterns increased and their width (FWHM) decreased with increasing annealing temperature, demonstrating the improvement in the crystallinity of the annealed films. Phase transformation at higher annealing temperature involves a competition among three events such as : grain growth of anatase phase, conversion of anatase to rutile and grain growth of rutile phase. AFM image of the as-deposited films and annealed films indicated exponential grain growth at higher temperature.

Keywords : TiO₂ thin film, nucleation and growth, spin coating.

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1. Introduction

Titanium dioxide (TiO₂) is one of the most promising and extensively investigated oxide materials in thin film form for broad range of applications [1]. TiO₂ in bulk form exists in three crystalline polymorphs [2] : Two tetragonal phases anatase and rutile and a third orthorhombic phase, brookite. The polymorphic transformation of TiO₂ is complex. There occurs both phase conversion as well as micro-structural modification on annealing at high temperatures [3]. The interdependency of these two events has led

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to a lot of controversy in the proposed phase transformation mechanism. While some authors [4,5] have proposed that the anatase to rutile phase transformation is a nucleation and growth process at the boundary of anatase phase, others [6,7] have indicated that with increasing annealing temperature, rutile nucleates within the anatase phase and grows in size consuming the surrounding anatase.

In the present study, we show that the phase transformation from anatase to rutile structure of titania in thin film form involves a competition among three events such as grain growth of anatase phase, conversion of anatase to rutile, and grain growth of rutile phase.

2. Experimental details

Thin films of TiO_2 were deposited by spin coating method using sol-gel technique. To prepare the coating solution, 5 ml of titanium isopropoxide (Aldrich, 99.9%) was dissolved in 30 ml of dehydrated ethanol. Then 0.26 ml of 60% nitric acid (Merck) and 0.31 ml of distilled water were added and stirred for 3 h. The substrates used were Si (100) wafer with a resistivity of $4 \text{ M}\Omega$. Before deposition, the substrates were thoroughly cleaned in an ultrasonic bath using propanol as a solvent. The deposited films were annealed at several temperatures in the range $400\text{--}1000^\circ\text{C}$ for 1 h.

Crystalline structure and particle size of the films were investigated by X-ray diffractometer (Bruker-D8) in a grazing incidence mode with $\text{Cu-K}\alpha$ radiation. Raman spectra were recorded using the 514 nm line of Ar^+ laser excitation using a Renishaw-INVIA Micro-Raman Spectrometer. The surface morphology was investigated using 'Nanoscope IIIA' atomic force microscope of Digital Instruments. All pictures were obtained in the tapping mode.

3. Results and discussion

The as-deposited films did not show any XRD peak of TiO_2 indicating amorphous nature. Two peaks (* marked in Figure 1), however, appear which do not correspond to any phase related to Ti or Si as seen from the respective JCPDS files. We presume that some organic phases, which are present during film growth by chemical route, contribute to the observed peaks. Since the organic phase is unstable at high temperatures, these peaks vanish in the annealed films. The anatase phase of TiO_2 evolves by annealing the films at 400°C and above (Figure 1). For 400°C annealed films, only the most intense peak of anatase structure corresponding to (101) reflection appears. Other peaks of anatase structure could not be detected since they were below the noise level. Annealing at higher temperature (700°C) leads to the growth of anatase phase and appearance of a large number of peaks corresponding to this phase. The diffraction pattern of the film annealed at 800°C contains peaks of both anatase and rutile phases, indicating the occurrence of transformation to rutile phase between 700 and 800°C . Complete transformation, however, could not be achieved even

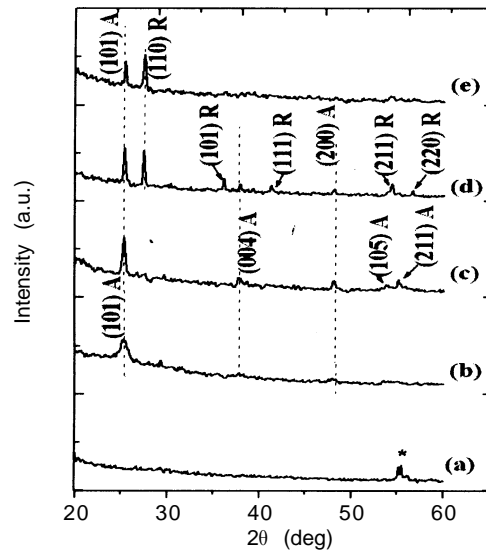


Figure 1. GAXRD patterns of the TiO₂ thin films on Si (100) wafers as a function of annealing temperature (a) 0°C (as-deposited), (b) 400°C, (c) 700°C, (d) 800°C and (e) 1000°C.

at 1000°C. Yamamoto *et al* [8] also observed that complete conversion of anatase to rutile does not occur even at 1100°C in epitaxially grown single crystalline TiO₂ thin films on SrTiO₃.

The crystallite sizes (D) of the prepared samples annealed at different temperatures were calculated from the FWHM of the most intense peaks of both the phases using Debye-Scherrer equation [9]. For anatase phase, annealing at high temperature seems to cause an increase in crystallite size (Figure 2) as expected. The crystallite size of rutile phase, however, decreases with increasing annealing temperature.

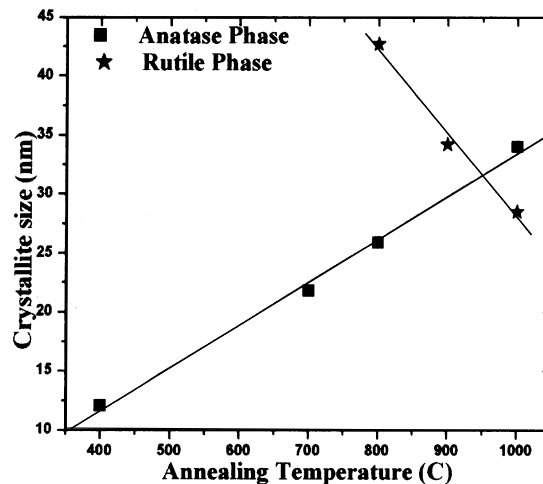


Figure 2. Evolution of anatase and rutile crystallite sizes with annealing temperature.

Temperature controlled heat and mass transport leads to the growth of anatase particles as is evident from the linear increase of the anatase crystallite size with increasing annealing temperature (Figure 2). Associated with the growth of anatase crystallites, anatase to rutile phase transformation has been argued to arise either at the grain boundary [4] or within the grains [6,7] of anatase. This occurs through a nucleation and growth process during which rutile nuclei form and grow in size by consuming the surrounding anatase. If the rutile nuclei form within the anatase crystallites, the grains of rutile crystallites can only increase with increasing annealing temperature. Our observation of the decrease in the rutile crystallite size with increasing annealing temperature thus points out to the mechanism of anatase to rutile phase transformation where rutile nuclei form on the surface of anatase particles [4,5]. With increase in the annealing temperature, the anatase crystallites grow bigger in size with a consequent reduction in the volume fraction of their grain boundary. Since the rutile phase nucleates at the grain boundary of the anatase phase, the reduced grain boundary volume fraction of the latter at higher temperature is expected to suppress the growth of the rutile crystallites (Figure 2). More than the crystallite size, the volume-fraction of the two phases decides the intensity of their XRD peaks. The reduced intensity of the anatase peaks for 1000°C annealed film (Figure 1) indicates that a large fraction of the anatase phase convert to rutile.

Figure 3 gives the Raman spectra of TiO₂ films annealed at different temperatures. A common feature in this figure is the appearance of the characteristic peaks of Si at 300, 520 and 950 to 980 cm⁻¹ [10]. Raman spectrum of the as-deposited TiO₂ film

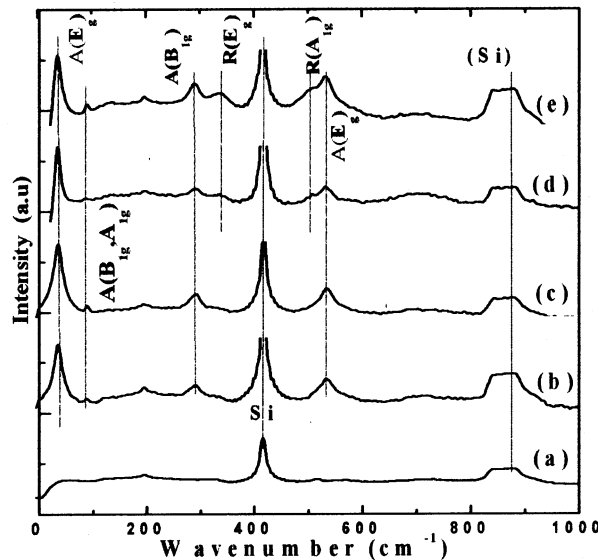


Figure 3. Raman spectra of the TiO₂ thin films on Si (100) wafers as a function of annealing temperature (a) 0°C (as-deposited), (b) 700°C, (c) 800°C, (d) 900°C and (e) 1000°C.

did not show any peak of the TiO₂ phases, which indicates the amorphous state of the film. GAXRD also revealed the amorphous nature of the as-deposited films. The 700°C annealed films showed clear Raman peaks corresponding to the anatase phase of TiO₂. The strong Raman peaks around 141, 395 and 636 cm⁻¹ were assigned to the E_g , B_{1g} and E_g LO-phonon modes of anatase structure, respectively by factor group analysis [10,11]. The weak peak at 195 cm⁻¹ corresponds to B_{1g} , A_{1g} LO-phonon modes. Almost all Raman allowed vibrational modes for anatase titania were observed. The formation of anatase structure on annealing titania at 700°C is also confirmed from the XRD result (Figure 1). No other peak corresponding to brookite or rutile phase was observed here. The Raman peaks due to the anatase phase become sharper and stronger on annealing the films at 800°C. Peaks due to rutile phase, however, could not be observed in the Raman spectra of the 800°C annealed film, though GAXRD clearly showed peaks of rutile phase in addition to anatase phase. Raman peaks due to rutile phase appear in 900°C annealed film, which intensify on further increasing the annealing temperature to 1000°C. The rutile peak position and assignment are shown in Figure 3. Though rutile phase evolves at the expense of anatase phase, the latter is still retained in considerable fraction at 1000°C. XRD also indicates the presence of both anatase and rutile phases for 1000°C annealed film.

The FWHM of the lowest-frequency line at 141 cm⁻¹ corresponding to the E_g Raman mode in anatase TiO₂ phase decreases with annealing temperature (Figure 4) and approaches the value (7 cm⁻¹) of the anatase phase in single crystals [12,13]. The decrease of line width with increasing annealing temperature implies growth of anatase crystallites as evidenced from the FWHM analysis of XRD peaks (Figure 2). FWHM analysis could not be done for rutile peaks due to their low intensities. AFM image of the as-deposited films (Figure 5) shows particles of less than 17 nm dia, which coalesce and grow to particles of 36 nm dia upon annealing at 700°C. Further,

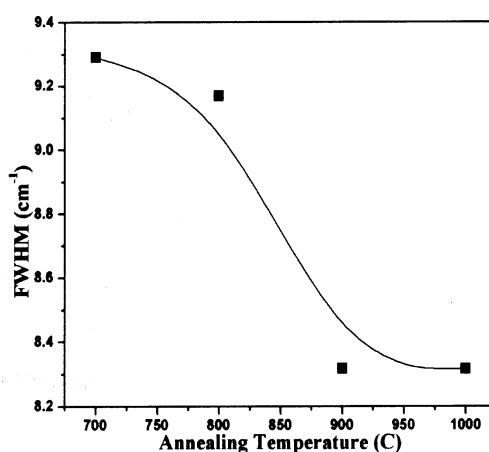


Figure 4. Variation FWHM of E_g (anatase) Raman mode of TiO₂ thin films as a function of annealing temperature.

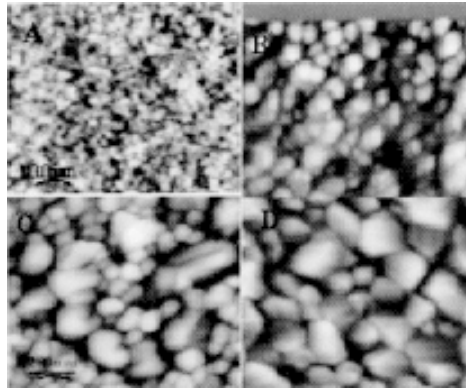


Figure 5. AFM images of the (A) as-deposited, (B) 700°C, (C) 900°C and (D) 1000°C annealed TiO₂ films.

annealing at 900 and 1000°C led to particles of ~118 and 300 nm, respectively. The grain size thus increases exponentially with annealing temperature (Figure 6). The as-deposited film has statistical RMS roughness value of ~0.7 nm, and exhibits a smooth surface. Like grain size, RMS roughness also increases exponentially with annealing temperature (Figure 7). The increase in the roughness is due to the grain

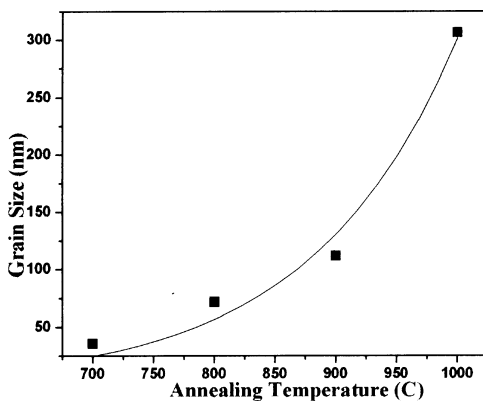


Figure 6. Grain size of TiO₂ thin film on Si (100) wafers as a function of annealing temperature.

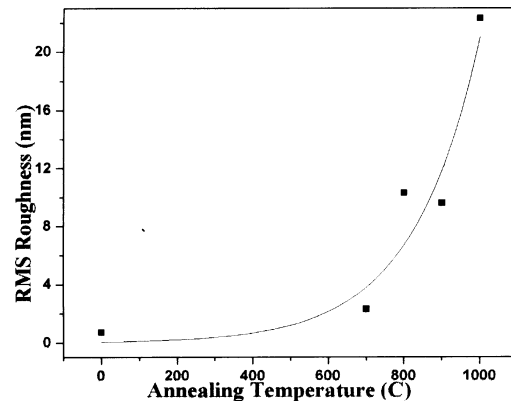


Figure 7. RMS roughness of TiO₂ thin films on Si(100) wafers as a function of annealing temperature.

growth as discussed earlier.

4. Conclusions

In a set of TiO₂ thin films, prepared by spin coating from titanium isopropoxide precursor, we show that annealing of the film leads to crystallization in the anatase structure above 400°C. Conversion of anatase to rutile phase starts in the temperature interval between 700–800°C. A fraction of the anatase phase, however, is still retained at temperature as high as 1000°C. Study of the grain growth of the two phases with

increasing annealing temperature indicates that the phase transformation from anatase to rutile structure of titania involves a competition among three events; grain growth of anatase phase, conversion of anatase to rutile and grain growth of rutile phase.

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