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Crystal Structure of TiO_2 Thin Films grown on Sapphire Substrates by RF Sputtering as a Function of Temperature

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This study investigated the dependence of crystal structure on growth temperature in the TiO_2 thin films deposited on c-, a-, and r-plane sapphire substrates by reactive RF magnetron sputtering. Deposition of the films was carried out at temperatures ranging from 400°C to 700°C. X-ray diffraction patterns revealed that TiO_2 with a rutile structure was epitaxially grown on substrates independent of substrate orientations. TiO_2 thin films were grown with a dominant peak of (200) on c-plane sapphire, and their crystallization and crystal quality were improved with growth temperature. For the films formed on a-plane and r-plane sapphires, the preferential orientation was [101]. However, the intensities of the (101) peak were very weak and were not dependent on growth temperature. The TiO_2 thin films formed on the sapphire had a band gap of about 3.7 eV, which was larger than that of bulk (3.03 eV).

Keywords: TiO_2 film, sapphire substrate, sputtering, growth temperature, crystal structure

1. INTRODUCTION

It is well known that TiO_2 thin films have high refractive index, high dielectric constants, good photocatalytic behavior, and high transmittance in the visible range. Thus, TiO_2 thin films have numerous applications for optical coating, electronic devices, photocatalysts, solar energy cells, and gas sensors. Many techniques including arc ion plating,[1] sputtering,[2] PLD,[3] MOCVD[4] and sol-gel[5,6] have been used to prepare TiO_2 films.

TiO_2 thin films have been deposited not only on semiconductor substrates, but also on oxide substrates, such as $LaAlO_3$, $SrTiO_3$, and quartz. Among oxide substrates, sapphire is very suitable due to its high stability and excellent crystalline quality.

The growth temperature has a significant effect on thin film properties such as physical (density, crystallization), electrical (resistivity, carrier concentration, and mobility), and optical (band gap, refractive index) properties.

In this paper, we demonstrate the effect of growth temperature on the crystal structures of TiO_2 thin films prepared on sapphire substrates with different crystallographic orientations. Surface morphologies and band gaps were also investigated.

2. EXPERIMENTAL PROCEDURE

Sapphire substrates with (110) a-plane, (001) c-plane, and (012) r-plane orientations were used. The substrates were ultrasonically cleaned in acetone, then methanol for 10 min each. Then the substrates were moved into the sputtering chamber with a TiO_2 target and heated to temperatures in a range of 400°C to 700°C. Argon and oxygen gases were injected as the sputtering and reaction gas, respectively. During the deposition, the substrate was rotated at 2 rpm in order to obtain uniform films. The crystal structures of the films were investigated with X-ray diffractometer (XRD) with Cu ká radiation. The band gaps of the films were estimated from optical transmission spectra obtained by UV-Vis-NIR spectrophotometer with a spectral range of 300-800 nm. The surface morphologies of the films were determined by field emission scanning electron microscopy (FESEM) operated at 30 kV.

3. RESULTS AND DISCUSSION

Figures 1, 2, and 3 show the X-ray diffraction patterns taken from the TiO_2 thin films deposited at temperatures in the range of 400°C to 700°C on c-, a-, and r-plane sapphire substrates, respectively. The TiO_2 thin films on c-plane sapphire substrates were grown with rutile [100] orientation normal to the substrate. The diffraction peak at $2\theta = 39.17°$

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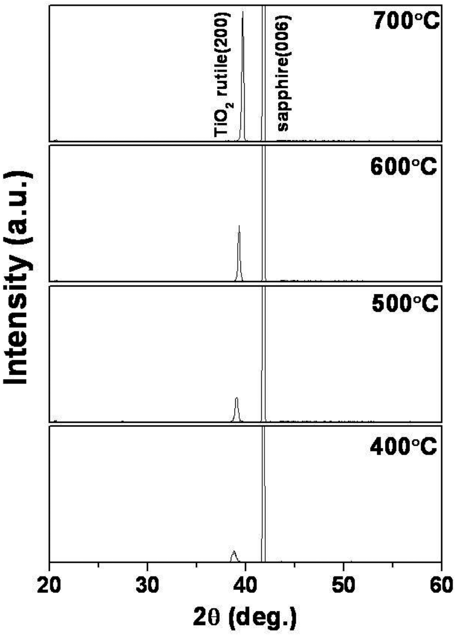

Fig. 1. XRD patterns of the TiO_2 films deposited on c-plane sapphire substrates at temperatures ranging from 400°C to 700°C.

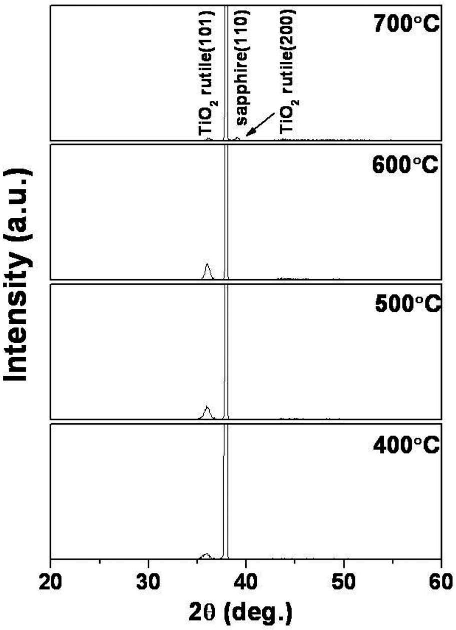

Fig. 2. XRD patterns of the TiO_2 films deposited on a-plane sapphire substrates at temperatures ranging from 400°C to 700°C.

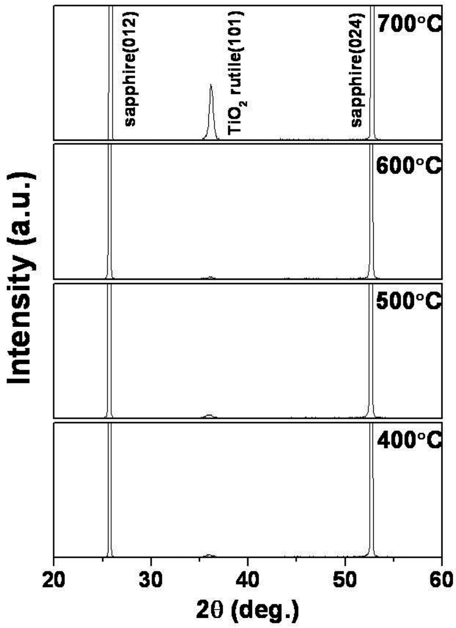

Fig. 3. XRD patterns of the TiO_2 films deposited on r-plane sapphire substrates at temperatures ranging from 400°C to 700°C.

(bulk $2\,\theta = 39.18°$) corresponds to the rutile (200) plane. The intensity of the rutile (200) peak increases with growth temperature, as shown in Fig. 1. The TiO_2 films prepared on a-plane sapphire substrates also have a rutile structure, but the peak from the rutile (101) plane is dominant (Fig. 2). The intensity of the rutile (101) peak is very weak even at a high temperature of 700°C. In addition, the peak from the rutile (101) plane is observed at $2\,\theta = 35.8°$, which is slightly shifted as compared with that of the bulk ($2\,\theta = 36.08°$). This suggests that lattice distortion is induced in the films. On the other hand, the peak from the (200) plane appears with the (101) peak at a temperature of 700°C. This demonstrates that the preferential growth orientation changes from the (101) plane to the (200) plane. As shown in Fig. 3, the XRD patterns show the peak intensity of the rutile (101) plane for the TiO_2 films formed on r-plane sapphire substrates. The intensity is very weak up to 600°C, but increases abruptly at 700°C, which indicates that the crystallization and the crystal quality of the film are improved at temperatures above 700°C. The crystallinity of the TiO_2 film on the c-plane sapphire substrate is improved with deposition temperature, while the TiO_2 thin films with high crystal quality are not fabricated on a- and r-plane sapphires even at high temperatures. Diffraction peaks from the rutile (101) plane in the TiO_2 films on the a- and r-plane sapphires are slightly shifted as compared with that of bulk, which indicates that the lattice distortion must lead to the deterioration of crystal quality.

Figure 4 shows the surface morphology of the TiO_2 thin films grown at 600°C on c-, a- and r-plane sapphire substrates, respectively. The SEM images show quite different morphologies depending on the substrate orientations. For the TiO_2 thin films on a- and r-plane substrates, no grain shape is observed on the surface, which means that the films have amorphous characteristics. However, the faceted grains are clearly observed on the TiO_2 film deposited on the c-plane substrate, which suggests that the film has a crystalline structure.

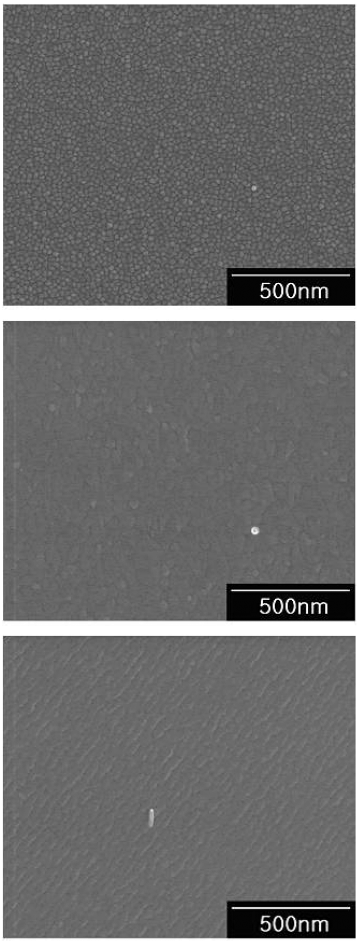

Fig. 4. SEM images of the TiO_2 films grown on (a) c-, (b) a-, and (c) r-plane sapphire substrates at 600°C.

The band gaps of the films were estimated by UV-Vis-NIR spectrometer. The optical band gaps (Eg) of the films were calculated by extrapolation methods from absorption edge. The absorption edge is given by

$$\alpha^2 = h\nu\text{-}Eg$$

where, h is Plank's constant, ν is the frequency of the incident photon and a is the coefficient of absorption. The coefficient of absorption, á, could describe as

$$I = I_0e^{-\alpha t}$$

where, I is the intensity of transmitted light, I_0 is the intensity of incident light and t is the film thickness. When I/I_0 is defined as the transmittance, α is obtained from $I = I_0e^{-\alpha t}$. The band gaps of the films were evaluated from the graph plotted according to $\alpha^2 = h\nu$. Figure 5 shows that the band gaps are independent on growth temperature and substrate orientation. The band gaps are estimated to be approximately 3.7 eV for all samples. This value is larger than that of the bulk rutile phase (3.03 eV). There are two possible reasons for the larger band gap[7]. One is an axial strain effect resulting from lattice deformation and the other is a change in the density of semiconductor carriers. Judging from the XRD patterns, the former probably played an important role in widening the band gap.

4. CONCLUSIONS

TiO_2 films with rutile structure were formed on c-, a-, and r-plane sapphire substrates by RF magnetron sputtering. The

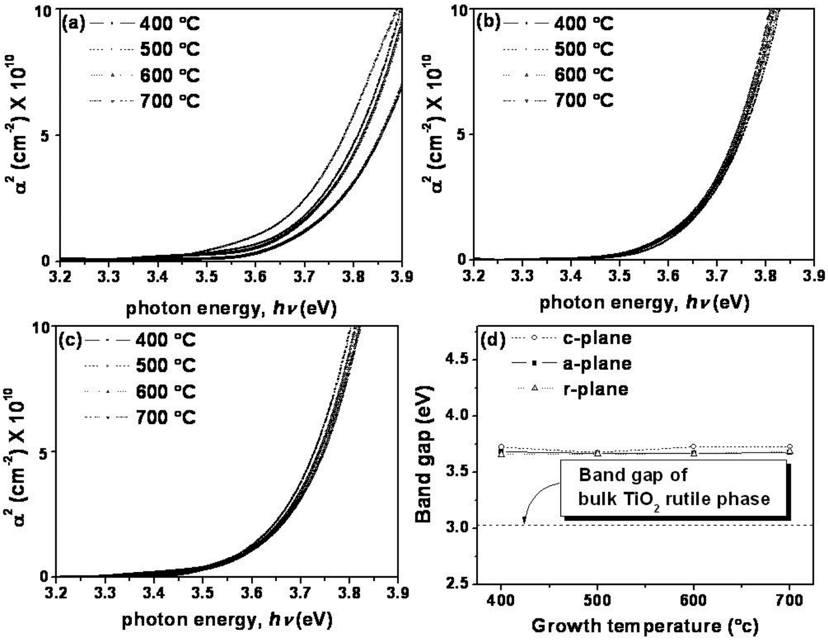

Fig. 5. Optical absorption spectra of the TiO_2 thin film deposited on (a) c-, (b) a-, (c) r-plane sapphire substrates at temperatures ranging from 400°C to 700°C, and (d) the band gaps of the films.

TiO_2 films prepared on c-plane substrates, showed a preferential growth orientation on the (200) plane. The TiO_2 films were also grown with a [101] orientation on a- and r-plane substrates. The film grown on the a-plane substrate showed a change in the preferential growth orientation from (101) to (200) at 700°C. On the r-plane substrate, a TiO_2 film with high crystallinity was obtained at temperatures above 700°C. All samples had a large band gap of about 3.7 eV.

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