Journal of Ceramic Processing Research. Vol. 13, No. 1, pp. 35~37 (2012)

JOURNAL OF
Ceramic Processing Research

Preparation and characterization of rutile TiO_2 films

Suparut Narksitipan[a,*] and Somchai Thongtem[b]
[a]*Division of Materials Science, Faculty of Science, Maejo University, Chiang Mai 50290, Thailand*
[b]*Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand*

Rutile titanium dioxide (TiO_2) films were prepared by calcination for 4 h at temperatures in the range 550-700 °C. Their structure and crystalline nature were investigated by X-ray diffraction (XRD), selected area electron diffraction (SAED) and Raman spectroscopy. After film preparation at 700 °C, rutile TiO_2 with a tetragonal structure was detected. Raman spectra displayed centered bands at 235, 440 and 603 cm^{-1}, corresponding to the rutile structure of TiO_2. The intensity of rutile TiO_2 increased with an increase in the calcination temperatures. The Raman spectra agree very well with SAED patterns. In addition, the characterization of rutile films with (scanning electron microscopy) SEM and atomic force microscopy (AFM) showed a surface roughness and dense particles with an angular shape.

Key words: Rutile films, Electron microscopy, X-ray diffraction.

Introduction

Among the numerous oxide materials, titanium dioxide (TiO_2) has received a great deal of interest due to its superior physical and chemical properties, including high stability. TiO_2 is one of the important inorganic materials in every day life, as a pigment for fabrics, for dye sensitizer solar cells, and as a catalyst. TiO_2 has been extensively investigated in recent years because of its many applications such as to purify air and water from contaminants [1-2], in gas sensors [3], and in solar cells [4]. TiO_2 as a thin film is able to be prepared by various techniques such as a sol-gel process [5], chemical vapor deposition [6], evaporation [7] and a sputtering method [8]. Among the three main crystal phases of TiO_2, rutile is the most thermodynamically-stable phase, but anatase and brookite have a high kinetic stability. However, rutile has some advantages over anatase such as a higher chemical stability, a high refractive index, a low production cost, etc. For this reason, in recent years there has been an increasing interest in preparation and characterization of TiO_2. It was the aim of the present study to investigate crystalline rutile films prepared by thermal oxidation at temperatures in the range 550-700 °C for 4 h. A further study has been made for the structure, crystallinity and surface morphology of the rutile films using X-ray diffraction (XRD), Raman spectroscopy, selected area electron diffraction (SAED), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

*Corresponding author:
Tel : +66-53-873-518
Fax: +66-53-878-225
E-mail: n_suparut@yahoo.com

Experimental

Rutile films were prepared samples (titanium sheet (99.6% at Ti)) 1.5 mm thick and cut into 10 mm × 10 mm test coupons. The samples were polished down to 0.3 μm with alumina powder and degreased with acetone. They were placed in a furnace, where the temperature was increased to 550, 600, 650 and 700 °C and held for 4 h in air. Finally, the samples were cooled down to room temperature and characterized. The structure and crystalline nature were characterized by X-ray diffraction (PHILLIP X'Pert) with Cu K_α radiation at 40 kV and 30 mA at scanning angles (2θ) from 10° to 100°. The Raman spectrum (HORIBA JOBIN YVON T64000) was analyzed in the range 200 to 1000 cm^{-1} and recorded using an Argon ion laser operating at 514.5 nm wavelength to determine the atomic vibrations. The morphological characterization of the films was performed by means of scanning electron microscopy (FE-SEM JSM-6335F), transmission electron microscopy (JEOL JEM-2010) and atomic force microscopy (Nano Scope ® IIIa by Veeco Digital Instrument).

Results and Discussion

Structure and crystallinity

After the preparation of films at calcination temperatures in the range of 550 to 700 °C for 4 h, crystallographic planes of the XRD spectra were indexed using Bragg's law for X-ray diffraction and compared with those of JCPDS software [9]. XRD patterns of a mixture of Rutile and oxygen-deficient TiO_2 are shown in Fig. 1. An XRD pattern from TiO_6 and Ti were detected in the films produced between 550 to 600 °C and the XRD pattern from TiO_6 indicated that the position and intensity of the characteristic peaks of the film is in good agreement with the JCPDS

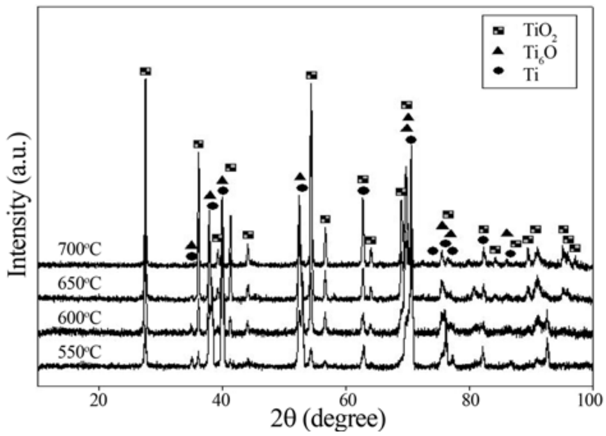

Fig. 1. XRD patterns of TiO_2 films produced at different temperatures.

file No. 72-1807, but amount of TiO_6 was quite low. The rutile TiO_2 phase appearing in the XRD patterns was confirmed with the JCPDS file No. 04-0551. The characteristic peaks of rutile were evident in samples prepared at 650 to 700 °C. The amount of the rutile TiO_2 phase increased with an increase in the temperature. Moreover, the detection of Ti shows that the X-ray beam penetrated the film, reflected the substrate underneath and refracted from the film layer. The EDX investigation, shown in Fig. 2, confirmed the formation of TiO_2 in these films. Ti and O peaks were detected-generated from rutile TiO_2 films. The EDX analysis is not able to differentiate between Ti of the films and of the substrate underneath. An SAED pattern of the film produced at a temperature 700 °C is shown in Fig. 3. The SAED patterns showed the brightness and intensity of polymorphic discrete rings of crystallites as shown in Fig. 3. The diffraction pattern was interpreted and indentified as tetragonal rutile TiO_2. When the films were prepared at a high temperature the intensity of the XRD pattern appeared shaper, which implied a higher of degree of crystallinity in these products. It is worth noting that the XRD and SAED analyses are in good agreement. Raman spectra are shown in Fig. 4. The rutile film prepared at a temperature of 700 °C had strong

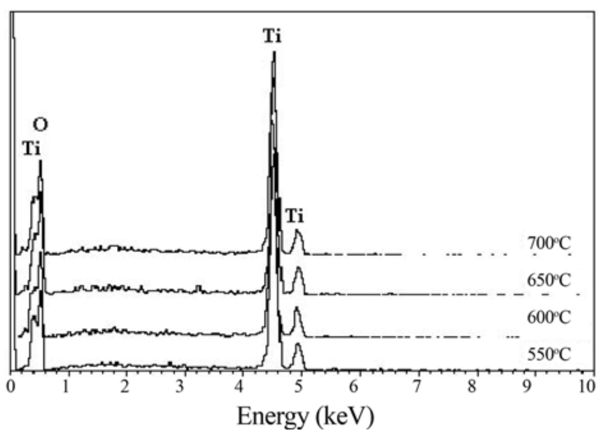

Fig. 2. EDX patterns of TiO_2 films produced at different temperatures.

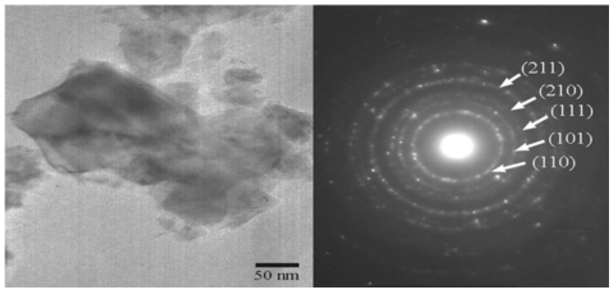

Fig. 3. TEM image and SAED pattern of a rutile TiO_2 film produced at 700 °C.

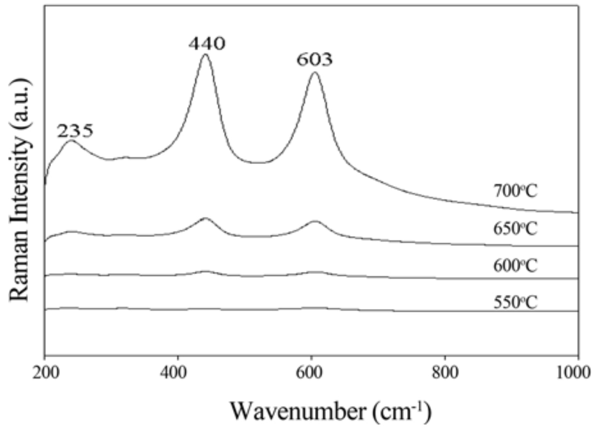

Fig. 4. Raman spectra of TiO_2 films produced at different temperatures.

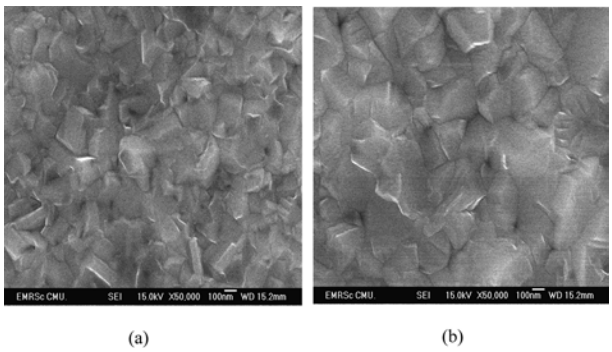

Fig. 5. SEM images of rutile films produced at (a) 650 °C and (b) 700 °C.

bands centered at 235, 440 and 603 cm^{-1} wavenumbers, which were assigned to be the rutile phase [10]. They were no longer detected at 500 °C. The presence of the rutile phase characterization by the Raman analysis is in good agreement with the characterization by SAED. Therefore, it was concluded that rutile TiO_2 was prepared at calcination temperatures between 650 to 700 °C.

Morphological analysis

As shown in Fig. 5, SEM images of rutile films were prepared at 650 and 700 °C for 4 h. They consist of dense particles with an angular shape. The particle sizes were in the range of 192 to 252 nm at calcination temperatures between 650 and 700 °C. As calcination temperature was

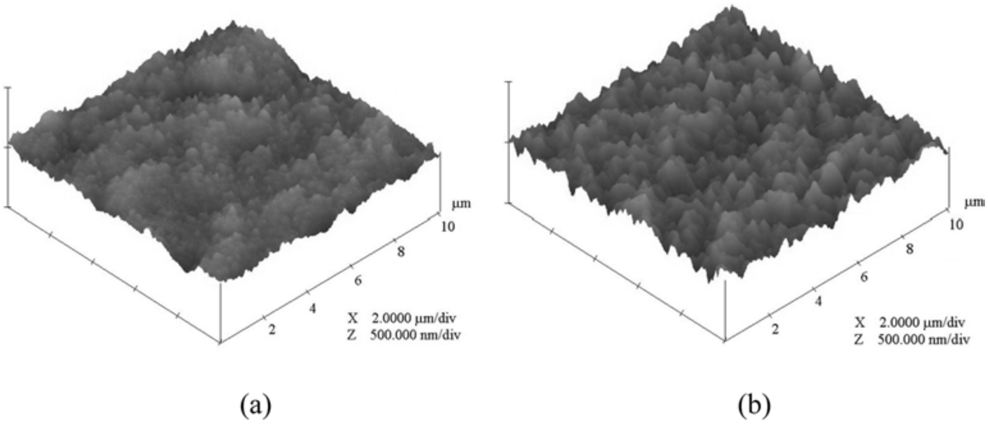

Fig. 6. AFM images of rutile films produced at (a) 650 °C and (b) 700 °C.

risen, the crystallite sizes were increased. A TEM image of the rutile TiO_2 film produced at 700 °C is shown in Fig. 3. The analysis was done at random on a surface of the film. The TEM image shows that the film was composed of well crystallized particles. The roughness on the surface was analyzed by AFM technique, which is shown in Fig. 6. The roughness values of films were increased from 22.530 to 44.503 nm as the calcination temperature was changed from 550 to 700 °C. The roughness values were increased with an increase in the calcination temperatures. It is worth noting that the TiO_2 film prepared at 700 °C is the roughest.

Conclusions

In conclusion, pure rutile TiO_2 films were successfully prepared at by calcination at 700 °C for 4 h. When the films were prepared at a high temperature, they are more crystalline and the XRD patterns appeared sharper. The effect of temperature on the structure of the films was discussed. The SAED and Raman spectra indicated that the film was confirmed to be tetragonal rutile TiO_2 with its characteristic structure. The roughness value was increased with an increase in the calcination temperature. At 700 °C, the product has the roughest surface-consisting of dense particles and an angular morphology.

Acknowledgements

We would like to give thank to the Thailand Research Fund (TRF), Thailand Toray Science Foundation and Faculty of Science, Maejo University for funding the research.

References

1. C.H. Ao and S.C. Lee, Chem. Eng. Sci. 60 (2005) 103-109.
2. L. Zhang, T. Kanki, N. Sano and A. Toyoda, Sep. Purif Tehnol. 31 (2003) 105-110.
3. E. Gyorgy, G. Socol, E. Axente, I.N. Mihailescu, C. Ducu and S. Ciuca, Appl. Surf. Sci. 247 (2005) 429-433.
4. K.M. Lee, C.W. Hu, H.W. Chen and K.C. Ho, Sol. Energ. Mat. Sol. C. 92 (2008) 1628-1633.
5. R. Mechiakh and R. Bensaha, C.R. Physique 7 (2006) 464-470.
6. B.C. Kang, S.B. Lee and J.H. Boo, Surf. Coat. Technol. 131 (2000) 88-92.
7. T. Miyata, S. Tsukada and T. Minami, Thin Solid Films 496 (2006) 136-140.
8. K. Eufinger, D. Poelman, H. Poelman, R.D. Gryse and G.B. Marin, Appl. Surf. Sci. 254 (2007) 148-152.
9. Powder Diffract. File, JCPDS Internat. Centre for Diffract. Data, PA 19073-3273, U.S.A., 2001.
10. S.J. Rigby, A.H.R.A. Obaidi, S.K. Lee, D. Mcstay and P.K.J. Robertson, Appl. Surf. Sci. 252 (2006) 7948-7952.