

Crystal properties of TiO₂ thin films grown at the low temperature regions by a reactive DC magnetron sputtering

H. Jee,¹ J. S. Kim¹ and H. W. Seo^{1,2*}

¹Department of Physics, Jeju National University, Jeju 63243, Republic of Korea

²Jeju National University Research Institute for Basic Science, Jeju 63243, Republic of Korea

Abstract

We have grown anatase-TiO₂ thin films in the low temperature ranges from RT to 300 °C by a reactive DC magnetron sputtering methods. In particular, we have focused on the crystalline properties of TiO₂ thin films dependent on the growth temperature. The increments in the crystallite size and population were found with an elevated temperature, which was revealed by x-ray diffraction and Raman spectroscopic methods. With the comparative study based on atomic force microscopic technique, we also identified the high quality of crystallites of the TiO₂ thin films.

PACS number: 61.43. -j, 68.55.-a, 81.15. Cd

Keywords: TiO₂, crystallites, growth temperature, thin films.

Email: hwseo@jejunu.ac.kr

Tel: +82-64-754-3512

Fax: +82-64-756-3506

I. Introduction

Since Fujishima found the photo-electrochemical water-splitting properties of titanium dioxides (TiO_2) under the UV illuminations, its adaption to photovoltaics, photocatalyst, and sensor devices have been actively pursued [1-3]. This intensive study leads to the commercial applications in the related fields [4]. The feasibility of fabrication process and the low cost fabrication becomes more important for enabling the practical utilizations. Recently, flexible electronics including electro-optical devices and bio-sensors have gotten special attentions as a next generation platform [5,6]. To realize TiO_2 as an element of flexible devices, the growth needs to be controlled below a certain temperature. The polyethylene terephthalate or polyethylene naphthalate plastic insulating films, which are typically used for the conductive template or substrate for the flexible electronics, becomes resistive and thermally-deformative beyond 200 °C [7].

A few groups have reported the physical vapour depositions of TiO_2 films, such as sputtering and atomic-layer deposition, at the low temperature regions [8-10]. However, their focus was limited mainly to the anatase-rutile phase transitions dependent on the growth temperature or its effects on the photo-catalytic performances. Note that the grain size and the related defects of films are also a crucial factor need to be considered. Especially, it is known that there is an optimal crystal or grain size to have the enhanced catalytic properties [11,12].

With this in mind, we paid attention to the low temperature growth of TiO_2 films by reactive DC sputtering methods. We then studied the structural properties of the as grown TiO_2 films, in terms of crystallite qualities and sizes.

II. Experimental Methods

We have grown TiO₂ thin films with 1 x 1 inch on glass substrate using a reactive DC magnetron sputtering. Target material used was pure titanium disk with 2 inches in diameter. Distance of target and substrate was maintained at 50 mm. Argon of 10 sccm and oxygen of 2 sccm were used as sputtering and reactive gas, respectively. The process pressure was kept at $\sim 4.6 \times 10^{-3}$ Torr. Plasma power of 150 W was used. The substrate temperature was changed from the room temperature (RT), 100, 200, to 300 °C.

After injection of argon gas, the plasma between the target and substrate was shielded by a shutter, and the pre-sputtering was performed. After the temperature was raised to the growth temperature and the target discharge impedance was stabilized, oxygen gas was injected. The shutter was then removed and the deposition was carried out for 10 minutes. The films were quenched to the RT after the deposition.

We monitored the crystal properties of the thin films using x-ray diffraction (XRD) (Empyrean, PANalytical) with *CuK α* radiation ($\lambda = 1.5406$ Å), and using the Raman spectroscopy (LabRAM HR Evolution, HORIBA) with Ar⁺ laser ($\lambda = 514$ nm). The Atomic force microscopy (Bruker, Multimode 8 AFM V) was used to scan the 0.5×0.5 μm range to verify morphology and roughness of the films. The thickness of thin film was measured with a Thin Film Thickness Measurement System (ST4000, K-MAC).

III. Results

Fig. 1(a) shows the Raman spectra obtained from the films grown with a different temperature from RT to 300 °C. The Raman peaks were observed at 143.5, 396.5, 517.9 and 639.0 cm⁻¹, which correspond to the five modes ($1A_{1g} + 2B_{1g} + 2E_g$) of anatase TiO₂ [13]. The peaks at 143.5 and 639.0 cm⁻¹ are attributed to $2E_g$ (ν_1, ν_5) mode while the peak at 396.5 cm⁻¹ is originated from $B_{1g}(\nu_2)$ mode. The peak at 517.9 cm⁻¹ are known to be combined $A_{1g}(\nu_3) + B_{1g}(\nu_4)$ modes [14], which is difficult to distinguish at room temperature but can be separated at a low temperature, ~73 K [15]. Note that $A_{1g}(\nu_3)$, $B_{1g}(\nu_4)$ and $E_g(\nu_5)$ are classified as stretching mode and, $E_g(\nu_1)$ and $B_{1g}(\nu_2)$ are bending mode.

[Fig. 1]

As the substrate temperature increases from RT to 300 °C, it was observed that the intensity of 143.5 cm⁻¹, $E_g(\nu_1)$, increases by 5.5 times, which reveals the improved crystal qualities and populations. Its full-width at half maximum (FWHM) decreases from 12.63 to 11.62 cm⁻¹, when the temperature is elevated to 200 °C, and increases again up to 12.1 cm⁻¹ at 300 °C, as shown in Fig. 1(b). The FWHM and shift of $E_g(\nu_1)$ peak are usually used to estimate the crystallite size, typically smaller than 20 nm, based on the phonon confinement effect [16]. However, any clear change both in FWHM and peak position were not observed, which is possibly due to no difference in crystallite size or overall bigger size of crystallites (> 20 nm).

To understand the crystallographic properties of the films dependent on the growth temperature, the XRD was investigated, as shown Fig. 2 (a). In comparison, Fig. 2(b) shows the XRD results of the 200 and 300 °C films in log scale, which were measured in a longer time scale, x 2.

[Fig 2]

As the temperature increases from RT to 300 °C, the XRD peak at $2\theta = 25.34^\circ$, anatase (101), becomes stronger, which agrees with the Raman results showing the gradual improvement of crystal qualities. The polycrystalline properties were also revealed. As growth temperature increases, the other 2θ peaks at 48.1° , 54.0° , and 55.1° were also observed, which are anatase phase of (200), (105), and (211).

Fig. 2(c) presents the intensity and FWHM of the peak (101) of $2\theta = 25.34^\circ$ vs. growth temperature. The average crystallite size was calculated from FWHM based on the Scherrer formula, $D = \frac{k \lambda}{\beta \cos\theta}$, where k is a dimensionless shape factor which is equal to 0.9, λ is the wavelength of $CuK\alpha$ radiation, 0.15418 nm, β is FWHM, and θ is the diffraction angle. The crystallites size was found to be 25.1 nm (100 °C), 25.7 nm (200 °C) and 31.6 nm (300 °C). The higher growth temperature leads to the bigger crystallite size, which is also inverse of the (101) peak intensity. The substrate heating enhances the surface migration of atoms and causes the better crystal qualities and the bigger size.

However, the XRD broadening can be caused not only by crystallite size effect but also by stain or strain-induced defects. To get an insight of this issue, we used the AFM methods and identified the physical crystallite size. The Fig. 3 shows the AFM scanning images of $0.5 \times 0.5 \mu\text{m}$. As the substrate temperature increased, the root-mean-square (RMS) roughness value

increased from 1.8, 2.11, 2.23 to 2.58 nm [Table 1]. Here, we categorize the crystallites into two groups; grain I (bright in images and bigger) and grain II (dark in images and smaller). We believe that the grain I is formed by the coagulation or Oswald-ripening of the grain II. The size of grain I increases from 21.8 to 28.2 nm when the growth temperature is escalated from RT to 300 °C, which are very similar to the results obtained from Scherrer's formula. In other words, the grain I are of good crystal qualities but the grain II may have poor crystal properties which may not attribute to the XRD peaks. In turns, this result confirmed that crystallites of grain I have negligible strain or defects.

[Fig. 3]

[Table 1]

We also studied the growth rate of the films. As the growth temperature increases to 200 °C, the growth rate decreases from 11.0 to 8.7 nm/min while the growth rate jumps to 10.4 nm/min at 300 °C. Here, we adapt the model of solid-state glass to crystallization [17], which is reasonable because 1) the melting temperature of Ti is quite high and 2) TiO₂ films grown at a low temperature are mainly amorphous. Temperature of the nucleation is typically lower than that of crystal growth [17], which can explain the growth rate having the minimum at the medium temperature, neither the highest or the lowest. In other words, the 200 °C is located beyond the nucleation temperature but below the crystallization temperature.

[Fig. 4]

IV. Conclusion

We have grown rutile-TiO₂ films at the low temperature regions from RT to 300 °C using reactive DC magnetron sputtering methods. Based on the comparative study of XRD and AFM results, we found that 1) the size of crystallites grows become bigger from 25.1 to 31.6 nm as the growth temperature increases from 100 to 300 °C and 2) they have negligible strain or defects. The growth temperature of 200 °C is expected to be between the nucleation and the crystallization temperature of rutile-TiO₂ films.

V. Acknowledgement

This work was supported by the 2018 scientific promotion program funded by Jeju National University.

V. References

- [1] A. Fujishima and K. Honda, *Nature* **238**, 37 (1972).
- [2] A. Hagfeldt and M. Graetzel, *Chem. Rev.* **95**, 49 (1995).
- [3] A. L. Linsebigler, G. Lu, and J.T. Yates, Jr., *Chem. Rev.* **95**, 735 (1995).
- [4] T. Ochiai and A. Fujishima, *JPPCAF. Rev.* **13**, 247 (2012).
- [5] S. R. Forrest, *Commun. Biol.* **428**, 911 (2004).
- [6] F. J. Pavinatto, C. W.A. Paschoal and A. C. Arias, *Int. J. Biosens. Bioelectron.* **67**, 553 (2015).
- [7] V. Zardetto, T. M. Brown and A. Di Carlo, *J. Polym Sci. B Polym Phys.* **49**, 638 (2011).
- [8] V. Senthilkumr, M. Jayachandran and C. Sanjeeviraja, *Thin Solid Films* **519**, 991 (2010).
- [9] K Safeen, V. micheli, R. Bartali, G. Gottardi and N. Laidani, *J. Phys. D: Appl. Phys.* **48**, 295201 (2015).
- [10] H. E. Cheng, C-M. Hsu and Y. C. Chen, *J. Electrochem. Soc.* **158**, D275 (2009).
- [11] N. Xu, Z. Shi, Y. Fan, J. Dong, J Shi and M. Z.-C. Hu, *Ind. Eng. Chem. Res.* **38**, 373 (1999).
- [12] A. J. Maira, K. L. Yeung 1, C. Y. Lee, P. L. Yue and C. K. Chan, *Catal. Commun.* **192**, 185 (2000).
- [13] G. D. Venkatasubbu, V. Ramakrishnan, V. Sasirekha and S. Ramasmy, *J. Exp. Nanosci.* **9**, 661 (2014).
- [14] T. Ohsaka, F. Izumi and Y. Fujiki, *J. Raman Spectrosc.* **7**, 321 (1978).
- [15] U. Balachandran and N. G. Eror, *J. Sol. Stat. Chem.* **42**, 276 (1982).
- [16] S. Balaji, Y. Djaoued and J. Robichaud, *J. Raman spectrosc.* **37**, 1416 (2006).
- [17] D. Savytskii, B. Knorr, V. Dierolf and H. Jain, *Scientific Reports* **6**, 23324 (2016).

[Table I] AFM results of TiO₂ films grown at RT to 300 °C

	RMS roughness (nm)	Crystallite size (nm)	
		Grain I	Gain II
RT	1.8	21.8	10.6
100 °C	2.11	22.7	12.5
200 °C	2.23	25.0	13.0
300 °C	2.58	28.2	13.9

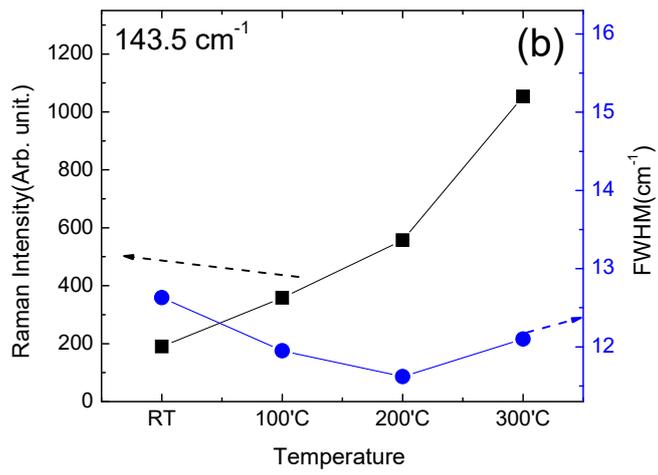
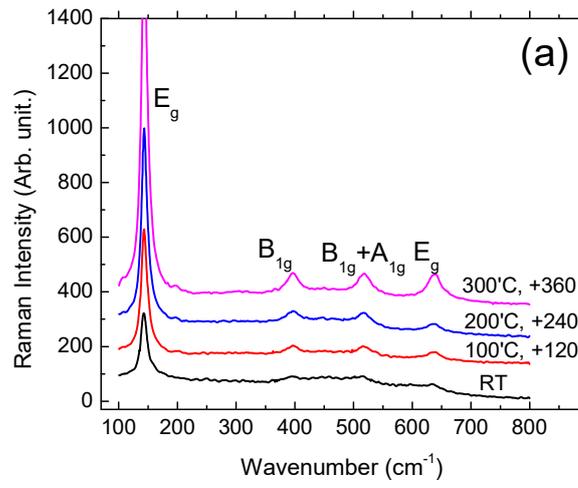
Figure Captions

[Fig. 1] (a) Raman spectra of TiO₂ films grown at RT to 300 °C, (b) Raman intensity and FWHM of the peak at 143.5 cm⁻¹ (*E_g*)

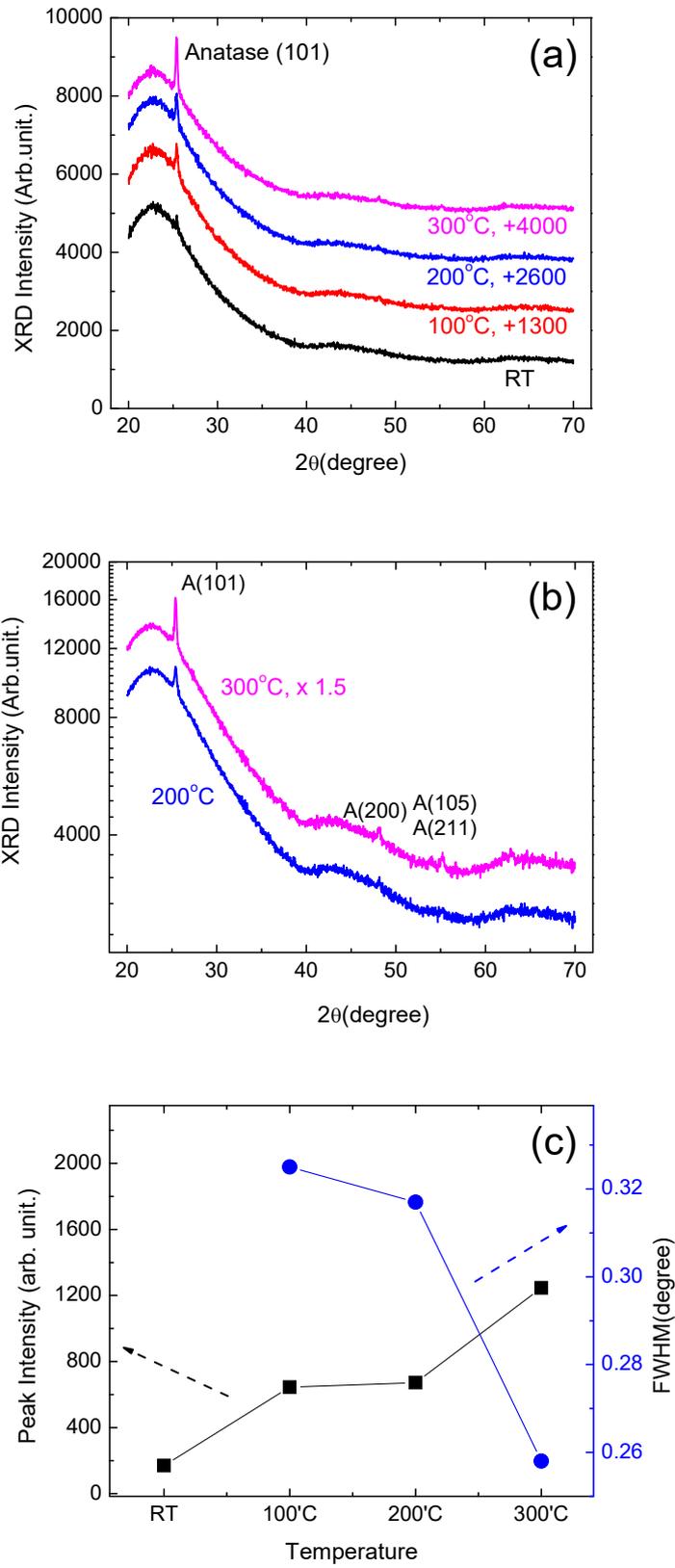
[Fig. 2] (a) XRD of TiO₂ films grown at RT to 300 °C, (b) XRD of TiO₂ films of 200 and 300 °C in a log scale, (c) XRD intensity and FWHM of the peak at anatase (101) vs. growth temperature

[Fig. 3] AFM images of TiO₂ films (0.5 x 0.5 μm) ; (a) RT, (b) 100 °C, (c) 200 °C, (d) 300 °C.

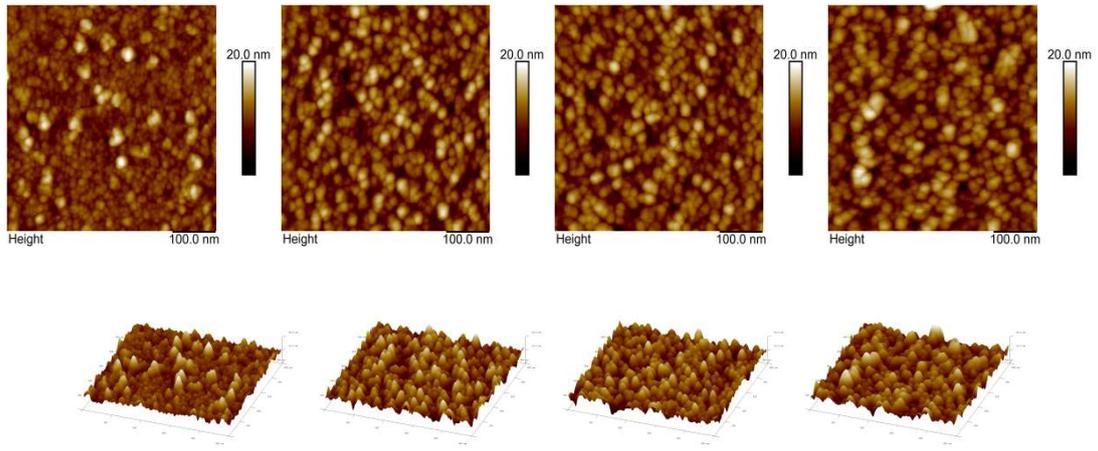
[Fig. 4] Growth rate of TiO₂ films vs. growth temperature



[Fig 1 (a,b)]



[Fig.2 (a,b,c)]



[Fig. 3 (a-d)]

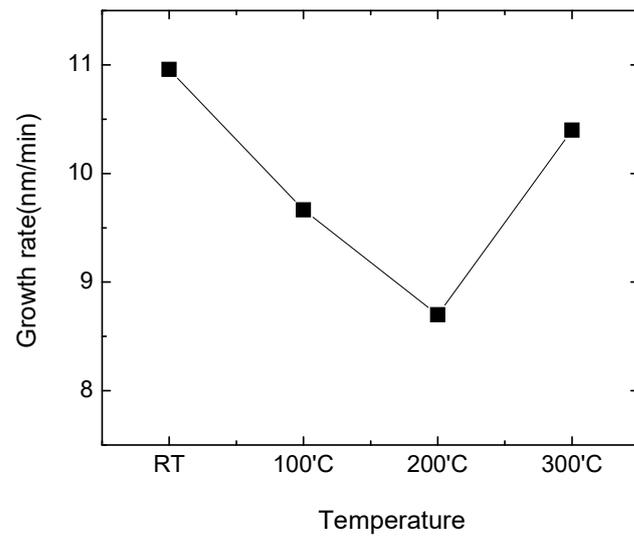


Fig. 4