

S. GOTO<sup>\*,#</sup>, Y. ADACHI<sup>\*</sup>, K. MATSUDA<sup>\*\*</sup>, M. NOSE<sup>\*\*\*</sup>

## CRYSTAL STRUCTURE AND OPTICAL PROPERTIES OF TiO<sub>2</sub> THIN FILMS PREPARED BY REACTIVE RF MAGNETRON SPUTTERING

### CHARAKTERYSTYKA CIENKICH WARSTW TiO<sub>2</sub> OTRZYMANYCH METODĄ REAKTYWNEGO ROZPYLANIA MAGNETRONOWEGO RF

In sputtering deposition process of TiO<sub>2</sub>, metal Ti or sintered TiO<sub>2</sub> target is used as deposition source. In this study, we have compared the characteristic of target materials. When TiO<sub>2</sub> target was used, stoichiometric TiO<sub>2</sub> films was deposited under the Ar atmosphere containing 1.0% of oxygen. The highest sputtering rate under this atmosphere was 3.9nm/min at 3.4W/cm<sup>2</sup>. But, sintered TiO<sub>2</sub> target is fragile and cannot endure higher density of input power than 3.4W/cm<sup>2</sup>. On the other hand, Ti target needs higher oxygen concentration (8%) in sputtering gas atmosphere for obtaining rutile/anatase. Even though Ti target can be input twice power density of 7.9W/cm<sup>2</sup>, the highest deposition rate for Ti target was 1.4/nm, which was ~35% of the highest rate for TiO<sub>2</sub> target. Then we have study out the composite target consisting of Ti plate and TiO<sub>2</sub> chips. Using the composite target, stoichiometric TiO<sub>2</sub> films were prepared in the rate of 9.6nm/min at 6.8 W/cm<sup>2</sup> under the atmosphere of Ar/2.5%O<sub>2</sub>. Furthermore, we have found that the TiO<sub>2</sub> films obtained from the composite target consisted of about 100% anatase, whereas TiO<sub>2</sub> films obtained from other target have rutile dominant structure. The optical band gap energy of the film is determined by using the Tauc plot. The calculated band gap energies for the films deposited by Ti target and composite target were 2.95 and 3.24eV, which are equivalent to that of rutile and anatase structure, respectively.

*Keywords:* TiO<sub>2</sub>, Rutile, Anatase, sputtering, XRD

W procesie nanoszenia TiO<sub>2</sub> metodą rozpylania, jako tarczy używano metalicznego Ti lub spiekane TiO<sub>2</sub>. W pracy dokonano porównania obu materiałów. W przypadku zastosowania jako tarczy TiO<sub>2</sub> przy nanoszeniu w atmosferze Ar zawierającym 1,0% tlenu otrzymano stechiometryczną warstwę TiO<sub>2</sub>. Największa uzyskana szybkość rozpylania w tej atmosferze wyniosła 3,9 nm/min przy gęstości mocy wejściowej 3,4 W/cm<sup>2</sup>. Jednak spiekany TiO<sub>2</sub> jest kruchy i nie wytrzymuje gęstości mocy wejściowej powyżej 3,4 W/cm<sup>2</sup>. Z drugiej strony, przy rozpylaniu z tarczy Ti konieczne jest zwiększone stężenie tlenu (8%) w atmosferze aby otrzymać fazę rutil/anataz. Mimo że tarcza Ti wytrzymuje gęstość mocy dwa razy wyższą niż TiO<sub>2</sub> (7,9 W/cm<sup>2</sup>), największa uzyskana szybkość rozpylania wyniosła 1,4 nm/min, co stanowi ~35% najwyższej szybkości uzyskanej dla tarczy TiO<sub>2</sub>. Zbadano także tarczę kompozytową składającą się z płyty Ti oraz wiórów TiO<sub>2</sub>. W przypadku zastosowania tarczy kompozytywnej, szybkość rozpylania wyniosła 9,6 nm/min przy mocy 6,8 W/cm<sup>2</sup> w atmosferze Ar/2,5%O<sub>2</sub>. Dodatkowo, warstwy TiO<sub>2</sub> otrzymane z tarczy kompozytywnej zawierały około 100% anatazu, podczas gdy w przypadku warstw otrzymanych z pozostałych tarcz dominowała faza rutilu. Szerokość przerwy energetycznej wyznaczono na podstawie wykresu Tauca. Obliczone wartości przerwy energetycznej wynosiły 2,95 eV dla podłoża Ti i 3,24 eV dla podłoża kompozytowego, co odpowiada wartością przerw odpowiednio dla rutilu i anatazu.

## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) has indicated photocatalytic activity [1]. TiO<sub>2</sub> has three types of crystallographic structures: rutile, anatase, and brookite. Among these structures anatase is well known for its higher photocatalytic characterization because of electron-hole (e-h) lifetimes [2]. Sputtering is one of the methods to fabricate TiO<sub>2</sub> films or coatings. Usually, metal Ti or sintered TiO<sub>2</sub> target is used as deposition source in sputtering deposition process. Ti target can be input high

power, however deposition rate lower than that of TiO<sub>2</sub> target due to reactive sputtering under a high oxygen content of atmosphere [3]. On the other hand, as TiO<sub>2</sub> target needs lower oxygen concentration in sputtering gas, the deposition rate is higher than that of Ti target [4]. However, sintered TiO<sub>2</sub> target is fragile and cannot endure higher density of input power. We propose the composite target consisting of Ti plate and TiO<sub>2</sub> chips. In this study, TiO<sub>2</sub> films prepared by three types of target, namely Ti, TiO<sub>2</sub> and the composite target, we have compared the characteristic of target materials.

\* GRADUATE SCHOOL OF SCIENCE AND ENGINEERING FOR EDUCATION, UNIVERSITY OF TOYAMA, 3190, GOFUKU, TOYAMA, JAPAN

\*\* GRADUATE SCHOOL OF SCIENCE AND ENGINEERING FOR RESEARCH, UNIVERSITY OF TOYAMA, 3190, GOFUKU, TOYAMA, JAPAN

\*\*\* FACULTY OF ART AND DESIGN, UNIVERSITY OF TOYAMA, TAKAOKA 933-8588, JAPAN

# Corresponding author: ikenolab@eng.u-toyama.ac.jp

## 2. Experimental procedure

TiO<sub>2</sub> thin films were deposited by differential pumping co-sputtering system (DPCS, ULVAC, RSSI-2T) [5]. The deposition was done using a Ti (99.99% purity) target, TiO<sub>2</sub> target and the composite target. The sputtering chamber was evacuated to a base pressure of about  $4 \times 10^{-4}$  Pa. Previous to the sputtering, the target was pre-sputtered to remove the residual oxide and other pollutants from the target surface. Square coupons (25 mm×25 mm) of Alkali-free glass (Corning Eagle#2000) and mirror-polished Si wafer were used as substrates. All the substrates were cleaned ultrasonically with acetone, ethanol and 2-propanol before sputtering deposition. The substrates were non-rotating and non-heating during the deposition films. Working pressure was kept 0.27Pa (TiO<sub>2</sub> target) and 1.0Pa (Ti, composite target) respectively.

Details of the deposition parameters are given in Table 1. A mixed gas of Ar and O<sub>2</sub> were used as the sputtering gas. The flow rates of Ar and O<sub>2</sub> gases were controlled by mass flow controllers. The crystal structure of the films was evaluated by X-ray diffraction (Philips X'pert system) using Cu-K $\alpha$  radiation with thin film method. Optical properties of the deposited TiO<sub>2</sub> films were studied using spectrometer (HITACHI U-3500) in the range between 200 and 2000 nm.

TABLE 1  
Deposition parameters of TiO<sub>2</sub> films

	TiO <sub>2</sub> target	Ti target	Composite target
Total pressure [Pa]	0.27	1.0	1.0
Power density [W/cm <sup>2</sup> ]	150	300	300
Oxygen concentration [%]	1.0	10	2.5
Deposition rate [nm/min]	3.9	1.4	9.6

## 3. Results and discussion

TiO<sub>2</sub> films were deposited under the Ar atmosphere containing 1.0% of oxygen. Sputtering rate under this atmosphere was 3.9nm/min at 3.4W/cm<sup>2</sup>. But the TiO<sub>2</sub> target got crack always, when the power density was increased over 3.4W/cm<sup>2</sup>. On the other hand, Ti target needs higher oxygen concentration in sputtering gas [3,6]. Even though Ti target can be input twice power density of 7.9W/cm<sup>2</sup>, the highest deposition rate for Ti target was 1.4/nm. Using the composite target, TiO<sub>2</sub> films were prepared in the rate of 9.6nm/min at 6.8 W/cm<sup>2</sup> under the atmosphere of Ar/2.5%O<sub>2</sub>. The XRD pattern of the films deposited at Ti, TiO<sub>2</sub> and the composite target are shown in Fig. 1. TiO<sub>2</sub> films deposited with Ti target, the films exhibits mainly rutile peaks. Using the TiO<sub>2</sub> target, the films exhibit intermixture rutile and anatase peaks. The TiO<sub>2</sub> films obtained from the composite target consisted of about 100% anatase peaks.

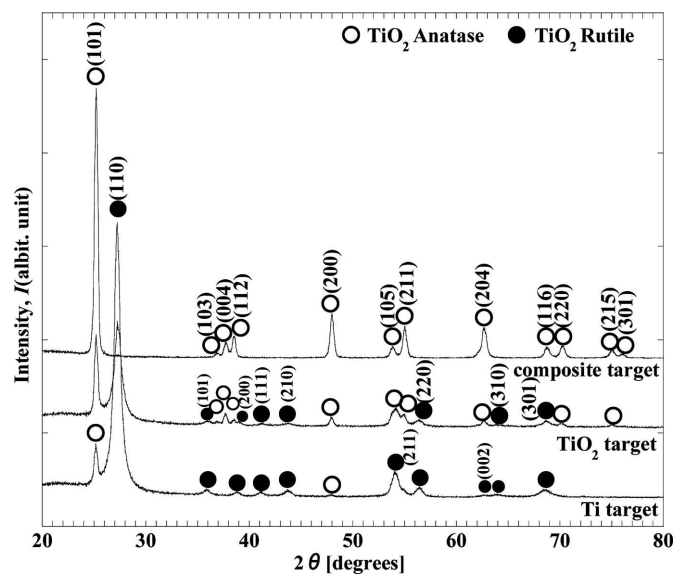


Fig. 1. X-ray diffraction patterns of TiO<sub>2</sub> films deposited at using different target

The optical bandgap energy of the film is determined by using the Tauc plot, and extrapolating the linear region of the plot toward low energies. Fig. 2 shows the variation of Tauc plot by the target materials. For bulk material, anatase has a higher optical bandgap of 3.2 eV while rutile has a lower optical bandgap of 3.0 eV [6-7]. The calculated band gap energies for the films deposited by Ti target was 2.95 eV. This is approximate value of the band gap energy of rutile. Other hand, the calculated band gap energies for the films deposited by the composite target was 3.24 eV. This is approximate value of the band gap energy of anatase.

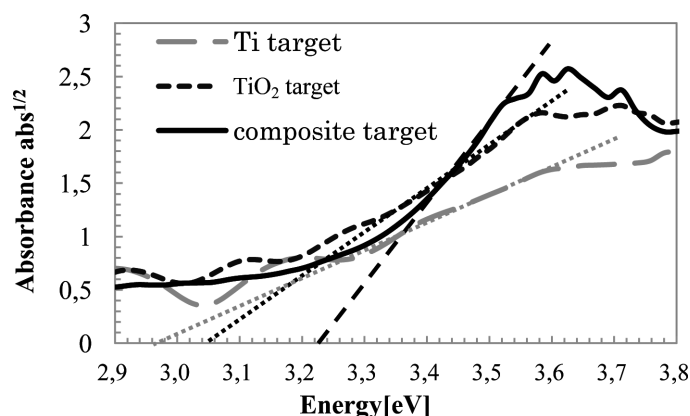


Fig. 2. Tauc plot of the TiO<sub>2</sub> films deposited at using different target

## 4. Conclusions

TiO<sub>2</sub> thin films were deposited on silicon and glass substrates by RF magnetron sputtering method using Ti target, TiO<sub>2</sub> target and the composite target. Using the composite target, TiO<sub>2</sub> films were deposited at the high sputtering rate of 9.6 nm/min under the atmosphere containing 2.5% oxygen. XRD pattern showed that the films obtained from the composite target had anatase single phase. Optical bandgap energy was approximate value of anatase phase at 3.2 eV.

## REFERENCES

- [1] A. Fujishima, K. Honda, *Nature* **238**, 37 (1972).
- [2] M. Xu, Y. Gao, E.M. Moreno, M. Kunst, M. Muhler, Y. Wang, H. Idriss, C. Wöll, *Phys. Rev. Lett.* **106**, 138302 (2011).
- [3] K. Tanamura, Y. Abe, K. Sasaki, *Vacuum*. **74**, 397 (2004).
- [4] D. Pjević, M. Obradović, T. Marinković, A. Grce, M. Milosavljević, R. Grieseler, T. Kups, M. Wilke, P. Schaaf, *Physica B.* **463**, 20 (2015).
- [5] M. Nose, T. Kurimoto, A. Saiki, K. Matsuda, K. Terayama, J. Vac. Sci. Technol. **30**, 1 (2012).
- [6] J. Xiong, S.N. Das, S. Kim, J. Lim, H. Choi, J.M. Myoung, *Surf. Coat. Technol.* **204**, 3436 (2010).
- [7] L. Miao, P. Jin, K. Kaneko, A. Terai, N.N. Gabain, S. Tanemura, *Appl. Surf. Sci.* **212-213**, 255 (2003).

*Received: 20 February 2014.*