A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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CRYSTAL STRUCTURE AND OPTICAL PROPERTIES OF TiO_2 THIN FILMS PREPARED BY REACTIVE RF MAGNETRON SPUTTERING

CHARAKTERYSTYKA CIENKICH WARSTW TiO_2 OTRZYMANYCH METODĄ REAKTYWNEGO ROZPYLANIA MAGNETRONOWEGO RF

In sputtering deposition process of TiO_2, metal Ti or sintered TiO_2 target is used as deposition source. In this study, we have compared the characteristic of target materials. When TiO_2 target was used, stoichiometric TiO_2 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^2. But, sintered TiO_2 target is fragile and cannot endure higher density of input power than 3.4W/cm^2. 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^2, the highest deposition rate for Ti target was 1.4/nm, which was ~35% of the highest rate for TiO_2 target. Then we have study out the composite target consisting of Ti plate and TiO_2 chips. Using the composite target, stoichiometric TiO_2 films were prepared in the rate of 9.6nm/min at 6.8 W/cm^2 under the atmosphere of Ar/2.5%O_2. Furthermore, we have found that the TiO_2 films obtained from the composite target consisted of about 100% anatase, whereas TiO_2 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_2, Rutile, Anatase, sputtering, XRD

W procesie nanoszenia TiO_2 metodą rozpylania, jako tarczy używano metalicznego Ti lub spiekanego TiO_2. W pracy dokonano porównania obu materiałów. W przypadku zastosowania jako tarczy TiO_2 przy nanoszeniu w atmosferze Ar zawierającym 1,0% tlenu otrzymano stechiometryczną warstwę TiO_2. Największa uzyskana szybkość rozpylania w tej atmosferze wyniosła 3,9 nm/min przy gęstości mocy wejściowej 3,4 W/cm^2. Jednak spiekany TiO_2 jest kruchy i nie wytrzymuje gęstości mocy wejściowej powyżej 3,4 W/cm^2. Z drugiej strony, przy rozpylaniu z tarczy Ti konieczne jest zwiększone stężenie tlenu (8%) w atmosferze aby otrzymać fazę rutyl/anataz. Mimo że tarcza Ti wytrzymuje gęstość mocy dwa razy wyższą niż TiO_2 (7,9 W/cm^2), największa uzyskana szybkość rozpylania wynosiła 1,4 nm/min, co stanowi ~35% najwyższej szybkości uzyskanej dla tarczy TiO_2. Zbadano także tarczę kompozytową składające się z płyty Ti oraz wiórów TiO_2. W przypadku zastosowania tarczy kompozytowej, szybkość rozpylania wyniosła 9,6 nm/min przy mocy 6,8 W/cm^2 w atmosferze Ar/2,5%O_2. Dodatkowo, warstwy TiO_2 otrzymane z tarczy kompozytowej zawierały około 100% anatazu, podczas gdy w przypadku warstw otrzymanych z pozostałych tarcz dominowała faza rutylu. 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 rutylu i anatazu.

1. Introduction

Titanium dioxide (TiO_2) has indicated photocatalytic activity [1]. TiO_2 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_2 films or coatings. Usually, metal Ti or sintered TiO_2 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_2 target due to reactive sputtering under a high oxygen content of atmosphere [3]. On the other hand, as TiO_2 target needs lower oxygen concentration in sputtering gas, the deposition rate is higher than that of Ti target [4]. However, sintered TiO_2 target is fragile and cannot endure higher density of input power. We propose the composite target consisting of Ti plate and TiO_2 chips. In this study, TiO_2 films prepared by three types of target, namely Ti, TiO_2 and the composite target, we have compared the characteristic of target materials.

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2. Experimental procedure

TiO_2 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_2 target and the composite target. The sputtering chamber was evacuated to a base pressure of about 4×10^{-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_2 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_2 were used as the sputtering gas. The flow rates of Ar and O_2 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_2 films were studied using spectrometer (HITACHI U-3500) in the range between 200 and 2000 nm.

TABLE 1

Deposition parameters of TiO_2 films

	TiO_2 target	Ti target	Composite target
Total pressure [Pa]	0.27	1.0	1.0
Power density [W/cm2]	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_2 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^2. But the TiO_2 target got crack always, when the power density was increased over 3.4W/cm^2. 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^2, the highest deposition rate for Ti target was 1.4/nm. Using the composite target, TiO_2 films were prepared in the rate of 9.6nm/min at 6.8 W/cm^2 under the atmosphere of Ar/2.5%O_2. The XRD pattern of the films deposited at Ti, TiO_2 and the composite target are shown in Fig. 1. TiO_2 films deposited with Ti target, the films exhibits mainly rutile peaks. Using the TiO_2 target, the films exhibit intermixture rutile and anatase peaks. The TiO_2 films obtained from the composite target consisted of about 100% anatase peaks.

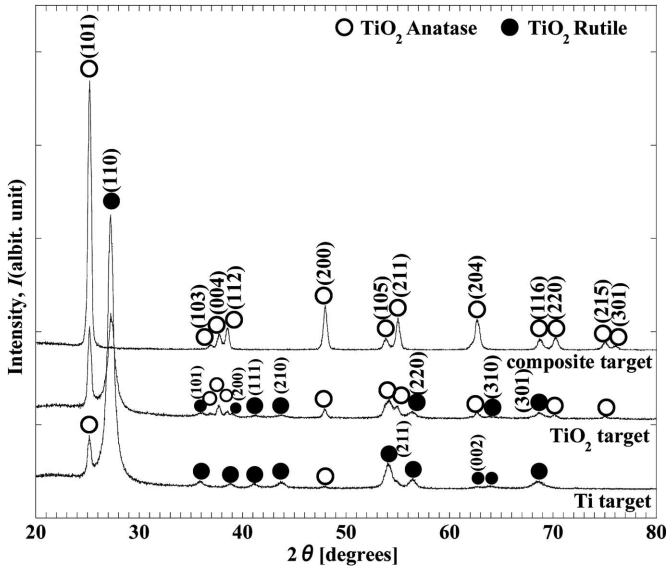

Fig. 1. X-ray diffraction patterns of TiO_2 films deposited at using different target

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.

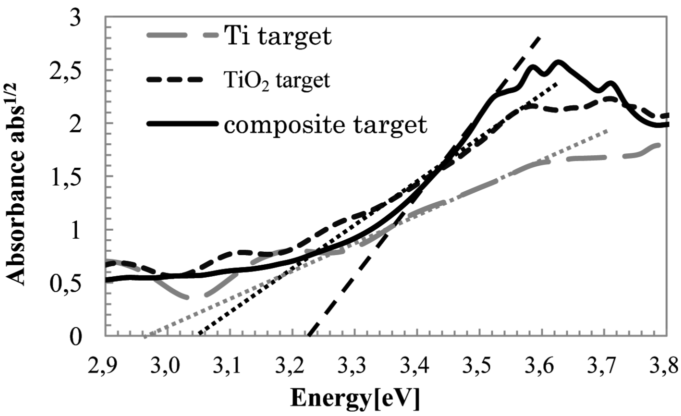

Fig. 2. Tauc plot of the TiO_2 films deposited at using different target

4. Conclusions

TiO_2 thin films were deposited on silicon and glass substrates by RF magnetron sputtering method using Ti target, TiO_2 target and the composite target. Using the composite target, TiO_2 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.

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