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STRUCTURE AND PHOTO- FUNCTIONAL PROPERTIES OF TiO_2 THIN FILM PREPARED BY RF HELICON MAGNETRON SPUTTERING

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ABSTRACT

Fabrication of titanium dioxide (TiO_2) thin film (200nm) has been done by using RF helicon magnetron sputtering from metallic Ti target under changing of O_2 flow rate and substrate temperature. Film structure was measured by X-ray diffraction (XRD). The films were examined by an X-ray photoelectron spectroscopy (XPS) to study the structure; atomic force microscopy (AFM) and field-emission scanning electron microscope (FE-SEM) were employed to investigate the surface morphology and the cross section of films, respectively. Optical properties and optical band gap were calculated by using UV-VIS spectrophotometer. Photocatalytic activity was evaluated by light induced degradation of methylene blue (MB) solution using UV and Vis light. TiO_2 thin film with a rutile phase at substrate temperature 100 ^oC and O_2 flow rate to 0.5 - 1.0sccm can be obtained, also an anatase phase can be fabricated when set substrate temperature to 300 ^oC and O_2 flow rate to 2.5sccm. Obtained films showed a high dense with smooth surface and high crystalline. Maximum degradation rate (about 85%) of MB has been indicated at anatase phase under UV light irradiation, while under Vis light irradiation rutile and anatase mixture phase showed a maximum degradation rate (about 15%).

In this work, the morphological, structural, optical, and photocatalytic properties of TiO_2 thin films that were fabricated by RF helicon magnetron sputtering under change of O_2 flow rate and substrate temperature have been investigated. It is expected that the change of substrate temperature and/or O_2 flow rate will make ability to control the film structure.

KEYWORDS: Titanium Dioxide, TiO2, Magnetron sputtering, and Photo-functional

التركيب البلوري والخصائص الضوئية لغشاء TiO2 المكون بطريقة بلازما الموجات اللاسلكية المغناطيسية

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الخلاصة

تم تصنيع مادة ثاني أكسيد التيتانيوم (TIO_2) (200 نانومتر) باستخدام تقنسة بلازما الموجات اللاسلكية المغناطيسية من معدن التيتانيوم في ظل تغير معدل تدفق O_2 ودرجة الحرارة الركازة. لفحص التركيب البلوري تم استخدام جهاز رسم حيود الاشعه السينية (XRD), ولفحص تركيب او مكونات الاغشية تم استخدام تقنية الاطياف الضوئية للاشعه السينية (XPS), في حين تم توظيف مجهر القوة الذرية (AFM) و المجهر الالكتروني الماسح (FE-SEM) لقياس تضاريس سطح والمقطع العرضي للاغشية. استخدم مطياف الاشعة المرئية والفوق البنفسجية (UV-VIS) لقياس الخصائص الضوئية وحساب فجوة الطاقة للاغشية. لفحص خاصية التحفيز الضوئي للاغشية تم غمرها في الميثيلين الازرق لمدة ست ساعات من ثم تعريضها لمصدر الضوء المرئي بطول موجي 665 نانومتر ومصدر اخر للاشعه الفوق بنفسجية, وبعدها تم قياس الفرق في امتصاص الضوء المرئي باستخدام جهاز النحليل الضوئي (SHIMADZU UV-2550).

تم الحصول على التركيب البلوري نوع (RUTILE) للاغشية التي صنعت عند حرارة 100 درجة و نسبة اوكسجين من 0.5 الى SCCM1.0, في حين التركيب البلوري (ANATASE) كان ظاهر عند رفع الحرارة الى 300 درجة ونسبة الاوكسجين لحد SCCM 2.5 , اظهرت نتئج الفحوصات اغشية ذات كثافة عالية و سطح املس وتركيب بلوري متماسك.

اقصى نسبة تحلل للميثيلين الازرق تحت الاشعة الفوق بنفسجية كان 85% للاغشية نوع (ANATASE) في حين ان النسبة انخفضت الى 15% تحت الاشعة المرئية للاغشية من النوعين (ANATASE) و (RUTILE).

1. INTRODUCTION

Titanium oxide (TiO_2) fundamentally is used in many applications because of its outstanding physical and chemical properties. Mainly, it shows a relatively high reactivity and high chemical stability under UV light. TiO_2 photocatalytic property shows an ability to decompose the environmental pollution materials (such as nitrogen oxide) by generating an active oxygen (O_2-, OH) when it is exposed to sunlight (Fujishima et al., 2000). Also, it is considered as one of harmless to the environment and inexpensive cost materials (Fujishima et al., 1999). This material has additionally great potential for the application to dye-sensitized photo-voltaic cell because of its interesting electrical and dielectric properties. It is expected to be used as element of a clean energy system in the near future. TiO_2 exists under two common and widely used different crystalline structures, which are Anatase-TiO_2 with 3.2eV band gap and Rutile-TiO_2 with 3.0 eV (Wagendristel and Wang, 1994).

Recently, most applications are using TiO_2 as thin film form (Wagendristel and Wang, 1994), which motivates an increasing number of researchers to prepare TiO_2 thin film by a range of techniques, such as wet technology processes like sol-gel and plating methods (Nagai et al., 2008 and Mechiakh et al., 2007), or dry process like chemical vapor deposition (CVD) (Nami et al., 1997), DC, and RF magnetron sputtering (Kee-Rong et al., 2006; Li et al., 2009; Maghanga et al., 2009; and Zeman and Takabayashi, 2002). However, TiO_2 thin film with a high density, smooth surface, and high photocatalytic property is still required by many researchers.

In this study, RF helicon magnetron sputtering with a metallic Ti target was used to fabricate TiO_2 thin film. RF helicon magnetron sputtering method is fashioned to work on conventional radio frequency (RF) magnetron sputtering, and the helicon waves are produced by an RF induced coil place in magnetron cathode. In this way, the plasma is held near the target in a small area which gives a number of advantages, such as stability of plasma discharge under low gas pressure, it can provide smooth films with a high purity and density, and also there is no direct contact between the substrate and plasma, so that the substrate temperature can be under control, additionally can provide a high crystalline film under low substrate temperature (Xinrong et al., 1999). Thus, it can be considered as useful way to fabricate a high dense TiO_2 thin film with controllable crystalline structure and high photocatalytic activity.

2. EXPEMINTAL DETAILS

2.1. Film preparation

TiO_2 thin films were prepared by using a multi-process coating system that is shown in Fig. 1 (ULVAC Inc.). Firstly, substrates were sputtered by Ar^+ ions for 10 minutes in order to clean the surface; this process has been done under Ar flow rate of 5sccm (standard cubic centimeters per minute) and the input power of 20W. Substrates were corning glass (corning #1737). Ti was sputtered under constant conditions of Ar gas flow rate (20sccm) and input power (100W). O_2 gas was inlet to film fabrication chamber in the vicinity of substrate under flow rate of 0.5, 1.0, 1.5, and 2.5sccm. The substrate temperatures were changed from 100, 200 to 300 ^oC. Ti deposition rate was measured by using QCM (Quartz Crystal Microbalance). Since O_2 flow rate of 2.5sscm showed a low deposition rate (Oxide mode), while O_2 flow rate of 0.5sccm showed a high deposition rate (Metallic mode) (Milam et al., 2005), then the formation time was set as shown in Table 1 to fix film thickness at 200nm.

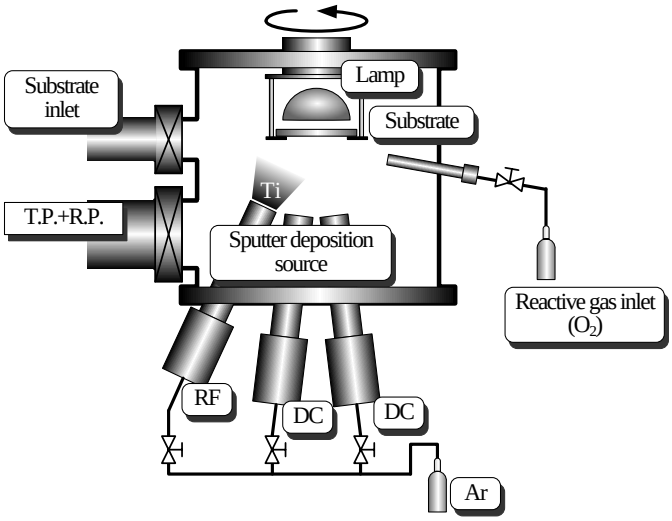

Fig. 1. Schematic diagram of multi-process coating system.

Table 1. Formation Time under Various O_2 Gas Flow Rates.

O_2 Flow Rate (sccm)	Ti Deposition Rate (nm/sec)	Formation Time (sec)
0.5	0.038	5263
1.0	0.034	5882
1.5	0.031	6451
2.5	0.006	33333

2.2. Measurements methods

The crystallization behavior of the TiO_2 thin films was analyzed by X-ray diffractions (XRD: High quality XG M18XCE, MAC Science Co., Ltd) using CuKα (0.154 nm) radiation under an incident angle of 0.3º. The surface morphology and roughness were observed by using atomic force microscope (AFM: SPM-9500, (Shimadzu Co.)) with tapping mode and under condition of 1μ m for scanning range and 2Hz for scan speed. Film cross section was investigated by Field Emission Scanning Electron Microscope (FE-SEM：S-480 Hitachi Tech. Co. Ltd.). Photocatalytic property was investigated by soaking a sample with area of 100mm^2 in methylene blue (MB) solution of 10 ppm in the concentration. UV light was irradiated to the sample by using a commercial sterilization lamp (1.180mW/cm^2). The change of a decolorized MB solution was measured by using spectrophotometer (UV-2550 Shimadzu Co.) at regular intervals.

3. RESULT S AND DISCUSSION

3.1. Structures

Fig. 2 a, b, and c show XRD patterns of TiO_2 thin films under various values of O_2 flow rate at a substrate temperature of 100, 200, and 300°C, respectively. The figures show that under all substrate temperature the films were changed from (110) orientation of rutile phase at 0.5 sccm to (101) orientation of anatase at 2.5 sccm.

Anatase phase fraction was calculated by using the formula (1) (Robert et al.) to understand how the TiO_2 phases transfer with change of O_2 flow rate.

$$AC(\%) = 100/(1+1.265\frac{I_R}{I_A}) \quad (1)$$

Where *AC* is the percentage portion of anatase in the mixture, while I_A and I_R are the integrated intensities of the (101) reflection of anatase and (110) reflection of rutile, respectively. Fig. 3 shows the anatase fraction vs O_2 flow rate under various substrate temperatures. From results, it is clear that under all substrate temperatures there is no anatase phase when the O_2 flow rate less than 1.5sccm, while the phase was changed to mixture phase at 1.5 and 2.5sccm. The influence of substrate temperature to structure was less than the O_2 flow rate effect. However, TiO_2 thin films with a single anatase phase can be obtained under O_2 flow rate of 2.5 sccm and substrate temperature of 300°C.

Another parameter can be calculated from XRD results by using Debye-Scherrer equation (2) (Jianging et al., 2000); this equation was used to calculate the average grain size (*d*) of deposited TiO_2 thin films as shown in Table. 2.

$$d_{hkl} = \frac{0.9\lambda}{\beta\cos\theta} \quad (2)$$

Where λ is an X-ray wavelength (1.54056Å) of Cu target, and β is the width at half maximum at (hkl) peak and θ is diffraction angle. The average grain sizes are in the range of 10.3 to 38.9 nm for (110) orientation of rutile phase and 8.3 to 67.1nm (101) orientation of anatase as listed in Table 2. It is noticed that in a low O_2 flow rate and under all substrate temperatures only (110) orientation of rutile phase was indicated as a main peak, and no anatase peaks can be indicated. 0.5sccm showed a rutile phase with slight lattice distortion causing a drooping in the average grain size, while in 1.0sccm the average grain was increased. Possibly the high deposition rate of Ti particles in metal mode (0.025nm/sec) comparing to that in oxide mode (0.006nm/sec) has a main role to yield rutile phase at low O_2 flow rate, Since there is tow conditions that should be found in the TiO_2 film formation of rutile phase which are higher concentration of the ionized excited species resulting from the higher electron temperature in the plasma, and another is higher energy of the particles impinging on the growing film surface (Yamagishi et al., 2003). From otherwise, total energy delivered to the growing film is responsible for its crystallization, thus the crystallization of the film improves with increasing this energy. Consequently, the increasing of O_2 flow rate was responsible for increasing of average grain size because the increasing in deposition time (Gribb and Banfield, 1997).

Additionally, it can be indicated from Table 2 that the increasing in substrate temperature, the structure was changed from mixture to anatase that is why the grain sizes of rutle phase were decreased from 38nm to 10nm with the increasing from 100 to 200 °C, respectively.

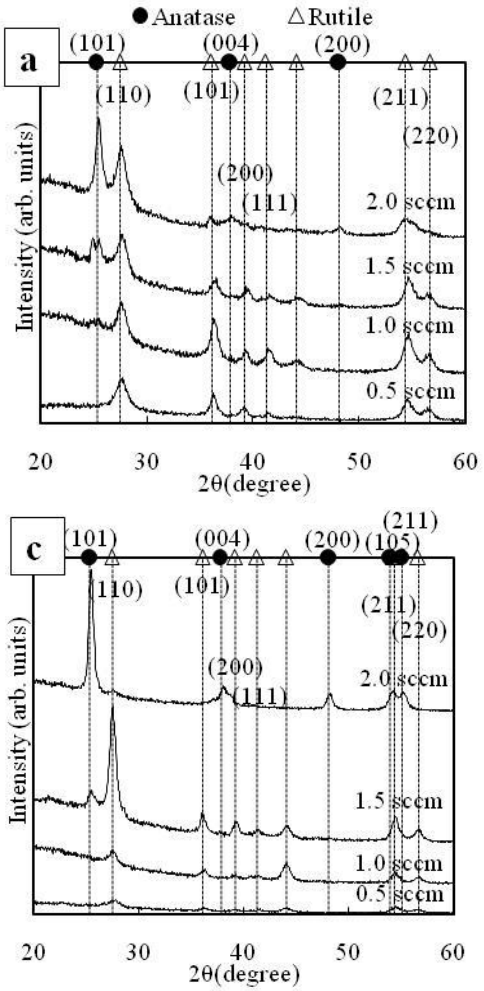

Fig. 2. XRD patterns for TiO2 thin films as function of an O2 flow rate at substrate temperature of (a) 100oC, (b) 200oC and (c) 300oC.

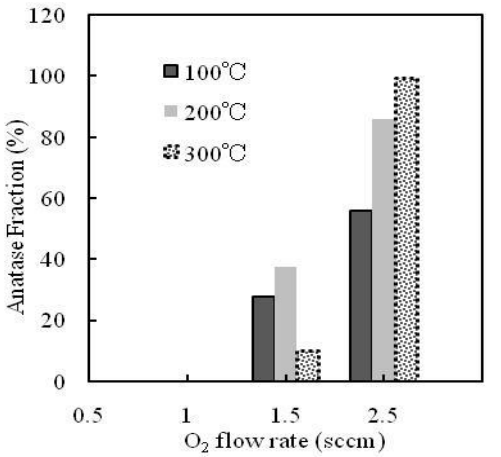

Fig. 3. Anatase fraction vs. O_2 flow rate under various substrate temperatures.

Table 2. Average Grain Size for all Samples

O_2 flow rate sccm	100 °C		200 °C		300 °C	
	d(nm)		*d*(nm)		*d*(nm)	
	R (110)	A (110)	R (110)	A (110)	R (110)	A (110)
0.5	25.0	-	10.3	-	17.0	-
1.0	35.6	-	32.8	-	32.3	-
1.5	35.6	25.0	38.9	25.0	38.9	28.4
2.5	38.9	47.7	22.3	47.7	10.0	57.0

3.2. Cross section and morphology

Fig. 4 presents a SEM micrograph cross section of TiO_2 thin films prepared under substrate temperature of 100°C and an O_2 flow rate of (a) 0.5sccm, (b) 2.5sccm. The increasing in an O_2 flow rate had no effect on film thickness or dense while it had a large effect to grain size. The cross-section micrograph reveals that each of the two samples showed high dense films

with thickness of 188 nm. Columnar grain structure films with size of 18-22nm and 58-60nm were observed in the sample that are prepared under low O_2 flow rate and high O_2 flow rate, respectively. This result showed an average grain size close to results that were calculated by Debye-Scherrer equation, which is about 25nm and 57nm, respectively.
Fig. 5 shows the morphology of TiO_2 thin films measured by AFM. The increasing of substrate temperature lead to an increasing in grain size, while films roughness (Ra) was increased slightly by increasing in O_2 flow rate and decreased by increasing of substrate temperature. TiO_2 thin films that are fabricated in this research showed a smooth surface comparing by that were formed by another method which refers to a homogenous and high dense thin film (Rawal et al., 2010 and Jung, 2004).

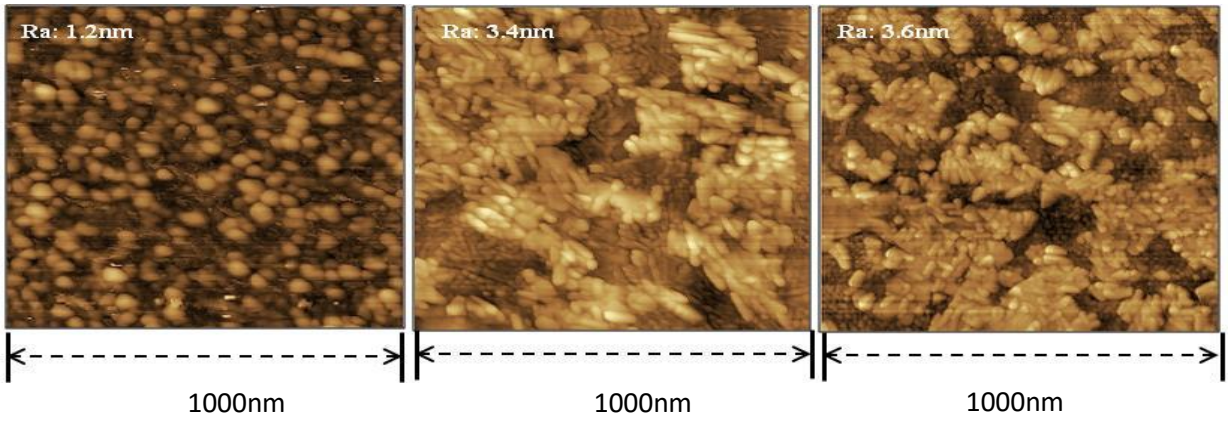

Fig. 4. SEM micrograph cross section of TiO_2 thin films prepared under substrate temperature of 100°C and an O_2 flow rate of (a) 0.5sccm, (b) 2.5sccm.

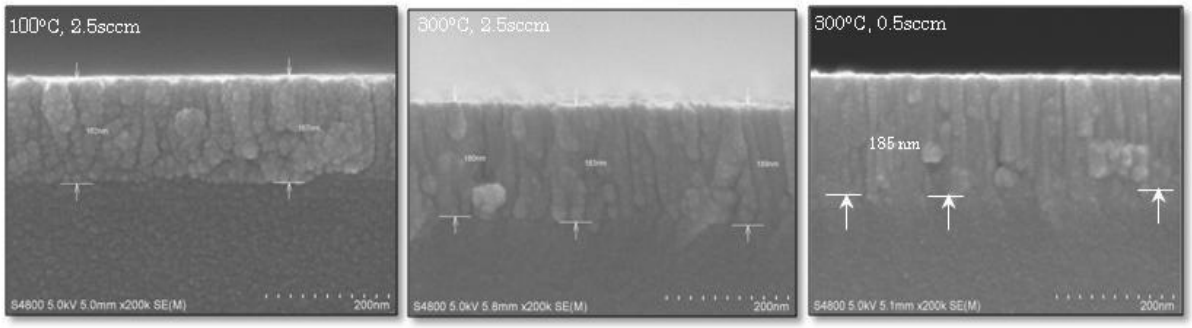

Fig. 5. Surface morphology of TiO_2 thin films measured by AFM under substrate temperature of 100°C and an O_2 flow rate of (a) 0.5sccm, (b) 2.5sccm.

3.3. Optical band gap

The absorption spectra of the TiO_2 thin films that are prepared in this work were measured as a function of the wavelength. The optical band gap (Eg) was determined from the absorption coefficient (α) using the Tauc relation (3) (Tauc et al., 1974).

$$\alpha = (hv - Eg)^{1/2} \quad (3)$$

Where *hv* is the energy of incident photon, and Eg is the value of the optical band gap corresponding to transitions indicated by the value r which is characteristic of the type of the optical transition process. Power parameter (r) has the value of 1/2 for a direct allowed optical transition and the value of 2 for an indirect allowed optical transition (Hegab et al., 1998). Since TiO_2 is direct band gap, in this work r estimated as ½ (Valencia et al., 2010). Fig. 6

shows the optical band gap of TiO_2 thin films as function of O_2 flow rate under substrate temperature of (a) 100, (b) 200, and (c) 300 ^oC. Under all substrate temperature the

samples that are prepared under O_2 flow rate of 0.5 and 1.0 sccm have a same rutile phase structure, while the sample that is prepared at 0.5sccm showed a band gap large than that was indicated at 1.0sccm. It is evident that the increasing in grain size that was happened by increasing O_2 flow rate from 0.5 to 1.0sccm associated by increasing in band gap, since the optical band gap correlated by films crystalline, grain size, surface morphology, etc (Li et al., 2006 and Domaradzki et al., 2006). Grain size effects band gap indicated when O_2 flow rate fixed and substrate temperature changed, such that 100^oC showed sample with band gap of 3.28eV while 300 ^oC showed 3.2eV under same 2.5 sccm in O_2 flow rate.

3.4. The photocatalytic property

As mentioned before, the photocatalytic property was investigated by soaking a sample with area of 100mm^2 in MB of 10 ppm in the concentration. Fig. 6a shows the light transmittance through MB at 664nm as function with O_2 flow rate. Light irradiation time was 6 hours for artificial sun light and 3 hours for sterilization light. High photocatalytic activity has been indicated at the samples that were formed under 1.0 and 1.5sccm. It's likely that the rutile phase presents with a close average grain size in these samples have a maximum photocatalytic property under visible light. Fig. 6b shows increasing in the photocatalytic property with increase of anatase concentration in structure. Maximum photocatalytic property was indicated at the sample that was fabricated under 2.5 sccm in O_2 flow rate and 300 ^oC in substrate temperature which showed a single anatase phase with 61.7nm in average grain size.

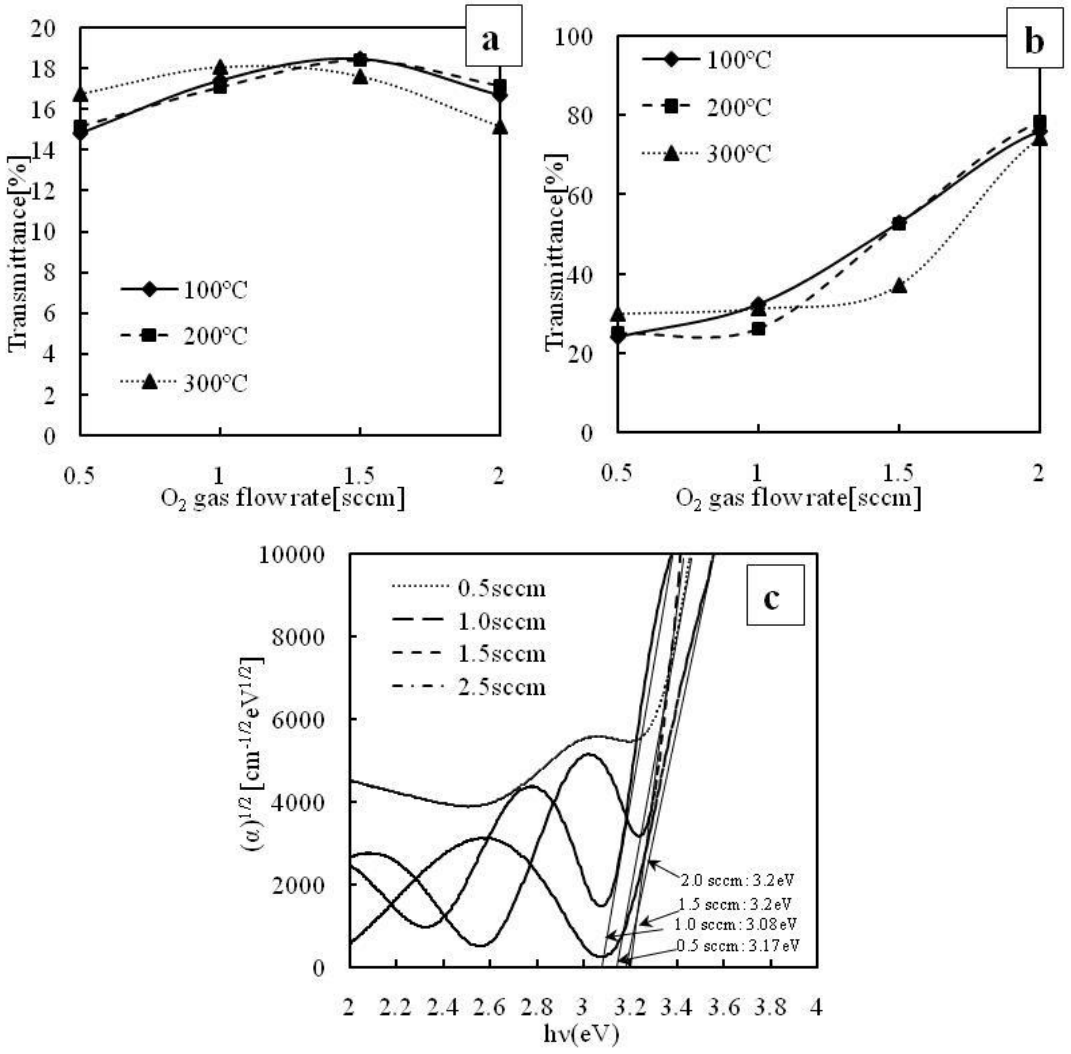

Fig. 6. Optical band gap of TiO_2 thin films as function of an O_2 flow rate under substrate temperature of (a) 10 °C 0, (b) 200 °C and (c) 300 °C.

4. CONCLUSION

The feasibility of fabricating TiO_2 thin film by helicon sputtering method can be summarized in many points, it can provide TiO_2 thin film with a high structural and simple control of films structural, and also it showed an excellent dense and homogenous film with a smooth surface. Helicon sputtering method can provide a rutile phase with band gap of 3.0eV under O_2 flow rate (1.0sccm) without the need to a high substrate temperature or to annealing process after formation process, this will be useful in an application that needs a low melting point substrate. Also, it can provide a high structural anatase phase with a band gap of 3.2eV less than 300 °C in substrate temperature and 2.5sccm in O_2 flow rate. Grain size of films is affected by the formation condition, and it has a significant effect on optical band gap. Photocatalytic property increased with increasing of anatase concentration in structure. Maximum photocatalytic property was indicated at the sample that was fabricated under 2.5 sccm in O_2 flow rate and 300 °C in substrate temperature which showed a single anatase phase with 61.7nm in average grain size.

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