บทที่ 5

สรุปผลการทดลอง

5.1 ฟิล์มของสารละลายของแข็งทองกับวาเนเดียม และทองกับวาเนเดียมออกไซด์ด้วยเทคนิคสปัตเตอร์ริงแบบกระแสตรง

- สามารถเตรียมฟิล์มของ Au, Au-0.25at%V, Au-0.65at%V, Au-1.4at%V, Au-2.2at%V และ Au-4.6at%V ด้วยเทคนิคสปัตเตอร์ริงแบบกระแสตรงได้ พบว่าค่าความต้านทานทางไฟฟ้ามีค่าสูงขึ้นเมื่อมีปริมาณของ V เพิ่มมากขึ้น และค่าความแข็งมีค่าเพิ่มขึ้นตามปริมาณของ V เช่นกัน

- สามารถเตรียมฟิล์มของ Au, Au-2.30at%VO_x และ Au-4.0at%VO_x ภายใต้บรรยากาศของก๊าซออกซิเจนเพื่อให้เกิดเป็นสารประกอบออกไซด์ของวาเนเดียมด้วยเทคนิคสปัตเตอร์ริง พบว่าค่าความต้านทานทางไฟฟ้าและค่าความแข็งเพิ่มสูงขึ้นตามการเพิ่มขึ้นของ V

- ผลจากการอบอ่อนที่อุณหภูมิ 200 และ 400 องศาเซลเซียส ส่งผลต่อค่าความต้านทานไฟฟ้า ทำให้ฟิล์มที่เตรียมนั้นมีค่าความต้านทานทางไฟฟ้าลดลง เมื่ออุณหภูมิที่ใช้ในการอบอ่อนสูงขึ้น เช่นเดียวกับค่าความแข็งของฟิล์มมีค่าลดลงเมื่ออุณหภูมิที่ทำการอบอ่อนเพิ่มสูงขึ้น

- จากการวิเคราะห์ด้วยเทคนิค XRD และ SAED บนฟิล์มของ Au-4.0at%VOx พบเฟสของทองบริสุทธิ์ แต่ไม่ปรากฏเฟสของ VOx เนื่องจากมีปริมาณค่อนข้างน้อย

และนอกจากนี้แสดงถึงความเป็นพหุผลึก (Polycrystalline) บนชั้นฟิล์มซึ่งแสดงให้เห็นจากรูปแบบการเลี้ยวเบนจากเทคนิค SAED

- ลักษณะทางสัณฐานวิทยาพบว่าชั้นฟิล์มประกอบด้วยอนุภาคขนาดเล็กระดับนาโน มีขนาดน้อยกว่า 100 นาโนเมตร

5.2 ฟิล์มของไทเทเนียมไดออกไซด์ (TiO_2)

- สามารถเตรียมฟิล์มไทเทเนียมไดออกไซด์ TiO_2 จากเทคนิคการเผาแคลไซน์ที่อุณหภูมิ 650 ถึง 700 องศาเซลเซียส เป็นระยะเวลา 4 ชั่วโมง

- ผลการวิเคราะห์ด้วยเทคนิค XRD และ SAED แสดงเห็นถึงการตรวจพบเฟสของรูไทล์ TiO_2 ซึ่งจากทั้งสองเทคนิคยืนยันการเกิดเฟสดังกล่าว และมีเฟสของรูไทล์ปริมาณเพิ่มขึ้นเมื่อเผาที่อุณหภูมิเพิ่มสูงขึ้น นอกจากนี้การวิเคราะห์ด้วยเทคนิคการกระเจิงแบบรามานแสดงสเปคตรัมที่มีความสอดคล้องกับเฟสของรูไทล์

- อนุภาคบนชั้นฟิล์มที่เตรียมได้มีขนาด192 ถึง 252 นาโนเมตร อนุภาคมีการจัดเรียงตัวค่อนข้างหนาแน่น และค่อนข้างหยาบ โดยวัดความหยาบมีค่าระหว่าง 22.530 ถึง 44.503 นาโนเมตร และที่อุณหภูมิ 700 องศาเซลเซียสจะมีความหยาบมากสุด

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Output ที่ได้จากโครงการวิจัย

งานวิจัยในโครงการนี้ผู้วิจัยมีความสนใจในการเตรียมฟิล์มของ Au-V และ Au-VOx โดยเทคนิคสปัตเตอร์ริง และเตรียมฟิล์มไทเทเนียมไดออกไซด์ด้วยเทคนิคการเผาแคลไซน์ที่อุณหภูมิต่างๆ ซึ่งมีOutput ที่ได้จากโครงการวิจัยซึ่งได้สรุปเป็นรายปีดังนี้

Output ในรอบ 1 ปี

ผู้วิจัยได้รับการตีพิมพ์ผลงานวิจัย จำนวน 1 เรื่อง มี Impact factor เท่ากับ 0.368

[1] **S. Narksitipan**, T. Bannuru, W. L. Brown, R. P. Vinci and S.Thongtem, Deposition of Au, Au–V and Au–VOx on Si wafers by co-sputtering technique, *Materials Science-Poland* 2009; **27**: 487-491.

Output ในรอบ 2 ปี

ผู้วิจัยได้รับการตีพิมพ์ผลงานวิจัยลงใน Conference proceeding ดังนี้

[1] **Suparut Narksitipan**, Characterization of Titanium Dioxide Nanoceramics Thin Films, *The 10th Russia/CIS/Baltic/Japan Symposiumon Ferroelectricity (RCBJSF10),* Yokohaman, Japan. June, 2010.

[2] **Suparut Narksitipan** and Somchai Thongtem, Preparation and characterization of Rutile TiO_2 nano thin films, *Organic and Inorganic Electronic Materials and Related Nanotechnologies*, Toyama, Japan. June, 2010.

[3] **Suparut Narksitipan** and Somchai Thongtem, *The influence of temperature on the phase compositions of titanium dioxide films, The 36 th Congress on Science and Technology of Thailand, Bangkok, Thailand.* October, 2010.

[4] **Suparut Narksitipan**, Influence of Oxygen Ions on the Structure of Titanium Oxide (TiO_x) Thin Films Prepared by Plasma Deposition Technique, The 28 th Annual

Conference of the Microscopy Society of Thailand, Chiang Rai, Thailand. January, 2011.

ผู้วิจัยได้ส่งผลงานวิจัยไปที่วารสารระดับนานาชาติ จำนวน 1 เรื่อง ซึ่งอยู่ในระหว่างการพิจารณารับ ดังนี้

[1] **ชื่อเรื่อง**: Preparation and characterization of rutile TiO_2 films

ชื่อวารสาร: Journal of Ceramic Processing Research

ผู้วิจัยได้นำเสนอผลงานทางวิชาการในที่ประชุมระดับนานาชาติจำนวน 2 ครั้ง ดังนี้

[1] **ชื่อการประชุม**: Russia/CIS/Baltic/Japan Symposium on Ferroelectricity (RCBJSF-10) ณ เมือง Yokhama ประเทศญี่ปุ่น

ชื่อเรื่อง: Characterization of Titanium Dioxide Nanoceramics Thin Films

[2] **ชื่อการประชุม**: Organic and Inorganic Electronic Materials and Related Nanotechnologies 2010 ณ เมือง Toyama ประเทศญี่ปุ่น

ชื่อเรื่อง: Preparation and characterization of Rutile TiO_2 nano thin films

ผู้วิจัยได้นำเสนอผลงานทางวิชาการในที่ประชุมระดับชาติ จำนวน 2 ครั้ง ดังนี้

[1] **ชื่อการประชุม**: The 36th Congress on Science and Technology of Thailand (STT 36) ณ กรุงเทพฯ

ชื่อเรื่อง: The influence of temperature on the phase compositions of titanium dioxide films

[2] **ชื่อการประชุม**: The 28th Annual Conference of the Microscopy Society of Thailand ณ จังหวัดเชียงราย

ชื่อเรื่อง: Influence of Oxygen Ions on the Structure of Titanium Oxide (TiO_x) Thin Films Prepared by Plasma Deposition Technique

ภาคผนวก

ภาคผนวก ก

ผลงานตีพิมพ์ระดับนานาชาติ

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Deposition of Au, Au–V and Au–VO_x on Si wafers by co-sputtering technique

S. NARKSITIPAN[1], T. BANNURU[2], W.L. BROWN[2], R.P. VINCI[2], S. THONGTEM[3*]

[1]Department of Physics, Faculty of Science, Maejo University, Chiang Mai 50290, Thailand

[2]Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015, U.S.A

[3]Department of Physics and Materials Science, Faculty of Science,
Chiang Mai University, Chiang Mai 50200, Thailand

Au, Au–V and Au–VO_x thin films were deposited on Si wafers by a co-sputtering technique. A four-point probe shows that the electrical resistivity of pure Au thin film on Si wafer without annealing is 7.2 mΩ·cm. The resistivities of thin films deposited on Si wafers, with or without annealing, tended to increase with the increase in the V and VO_x concentrations, and were attributable to the inhibited drift mobility of charge carriers within the films. By using the nanoindentation technique, the hardness in all cases also tended to increase with the increase in the V and VO_x concentrations. The hardness of pure Au, without annealing, was 2.52 GPa. It decreased to 1.80 GPa and 1.75 GPa after annealing at 200 °C and 400 °C, respectively. SEM and TEM analyses revealed the presence of nanosized particles on the surfaces of the thin films. XRD analysis of Au–4.00% VO_x film deposited on Si wafer detected the presence of Au, VO and Si. However, SAED analysis only detected the presence of Au on the film.

Key words: *Au, Au–V, Au–VO_x thin films; electrical resistivity; hardness*

1. Introduction

The development of biological and microelectromechanical systems (MEMS), microelectronics and optoelectronics has been increasingly important, inspiring a number of researchers to investigate new materials for use as thin films [1–3]. Low electrical resistivity, good resistance to wear, and biological compatibility are the prime features of such materials [1, 2]. Among various thin films, Au/Si is widely used due to its chemical stability, low resistivity, good reliability and other factors. These properties, influenced by microstructures and processing temperatures [4], deserve further investigation. Au and its alloys are very attractive for use in many MEMS devices due to

*Corresponding author: schthongtem@yahoo.com; sthongtem@hotmail.com

their low electrical resistivity and good corrosion resistance [1, 2]. Au thin films were deposited on substrates using various methods, such as Au films deposited on glass by ion beam-induced enhanced adhesion [5], nanoparticle Au films by pulsed laser deposition [6], uniform Au film on glass by microwave-assisted deposition [7], Au thin films by Ar sputtering [8] and by thermal evaporation [9], Pt and Au thin films by filtered vacuum arc [10] and Au films by electrodeposition [1]. V is a promising element which can be used as an alloying element of Au [2]. The electrical properties of VO_x are also very attractive. They change between metallic and insulating behaviours, termed metal–insulator transition (MIT) [11, 12]. VO has metallic conductivity due to the overlapping of 3d orbitals of the metal [12]. VO_2 exhibits phase change from insulator to metallic state at 68 °C, and V_2O_5 does so at 250 °C [11]. V_2O_3 undergoes phase transition from semiconductor to metal at –123 °C [13]. It has a low noise property due to its low resistivity at room temperature [13]. Therefore, VO_x film can be used for many applications such as electronic switches, sensors and memory units [11]. The purpose of the research was to deposit Au, Au–V and Au–VO_x thin films on Si wafers by the co-sputtering technique and to investigate their properties.

2. Experimental

Au, Au–V and Au–VO_x thin films were deposited on Si wafers by dc magnetron sputtering under the pressure of 4×10^{-3} torr Ar pressure. To deposit the Au–V and Au –VO_x films, two guns were used to control the Au and V compositions. The pressure of O_2 equal to 10^{-4} Torr was also applied to the Au–VO_x film depositions. Each film was deposited until it was 500 nm thick. A part of the deposited films were subject to annealing at 200 °C and 400 °C for 1 h. In order to characterize the resistivity, hardness, morphology and phase compositions of the deposited films, the following techniques were employed: a four-point probe method, a nanoindentation technique, X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and selected area electron diffraction (SAED).

3. Results and discussion

The electrical resistivities of Au and Au–V thin films deposited on Si wafers (Fig. 1a) increased with the increase in the V concentrations. These observations show that the additional V atoms hindered charged carriers from drifting in the films. The resistivities of pure Au thin films, with or without annealing at 200 °C and 400 °C, share the same values, namely 7.2 mΩ·cm. For the same V concentrations, their resistivities tended to decrease after high temperature annealing, especially at 400 °C. During the annealing, Au and V atoms were arranged in a systematic array, leading to a decrease in resistivity. The resistivities of Au, Au–2.30% VO_x and Au–4.00% VO_x (Fig. 1b), with or without annealing, slowly increased with the increase in the VO_x

content, and tended to decrease after the annealing. For each of the annealing temperatures, the resistivity of Au–VO_x is not as great as that of Au–V. The resistivities of Au–4.00% VO_x are almost equivalent to those of the corresponding VO_x –free matrix. They are 17.3 mΩ·cm if the sample is not subject to annealing (T_R), whereas it measures 17.7 and 10.2 mΩ·cm if subjected to annealing at 200 °C and 400 °C, respectively.

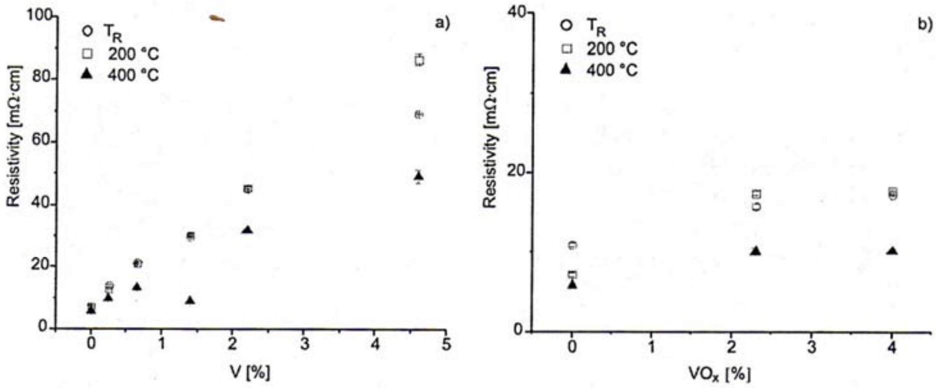

Fig. 1. Resistivities of Au, Au–V (a), and Au–VO_x (b) thin films deposited on Si wafers before (room temperature, T_R), and after annealing at 200 °C and 400 °C for 1 h

The hardness of each thin film deposited on Si wafer was measured ten times. Averages and standard deviations have been calculated (Fig. 2). The hardness of various Au and Au–V thin films (Fig 2), with or without annealing, tended to increase with the increase in the V concentrations. The hardness of pure Au not subject to annealing amounted 2.52 GPa, whereas after annealing at 200 °C and 400 °C it was

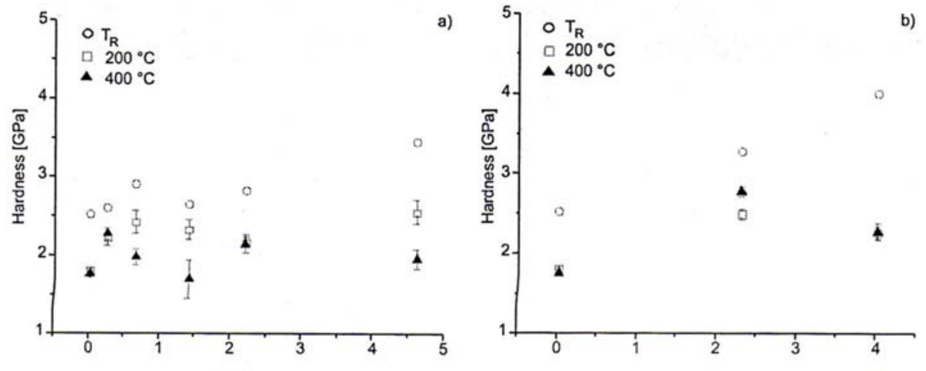

Fig. 2. Hardness values of Au, Au–V (a) and Au–VO_x (b) thin films deposited on Si wafers before and after annealing at 200 °C and 400 °C for 1 h

1.80 GPa and 1.75 GPa, respectively. In comparison with the values obtained for non-annealed films, the hardness of the corresponding thin films deposited on Si wafers became lower after annealing, due to the grain growth and phase change processes. In general, the lowest hardness corresponds to the highest annealing temperature. In the case of Au, Au–2.30% VO_x and Au–4.00% VO_x (Fig. 2b), the hardness also tended to increase with the increase in the VO_x concentration. The greatest hardness, equal to 4.00 GPa, was found in non-annealed Au–4.00% VO_x. The higher hardness implies that VO_x particles have the effect of hindering plastic deformation of thin films, by trapping dislocations. The hardness became lower when the films were subject to annealing.

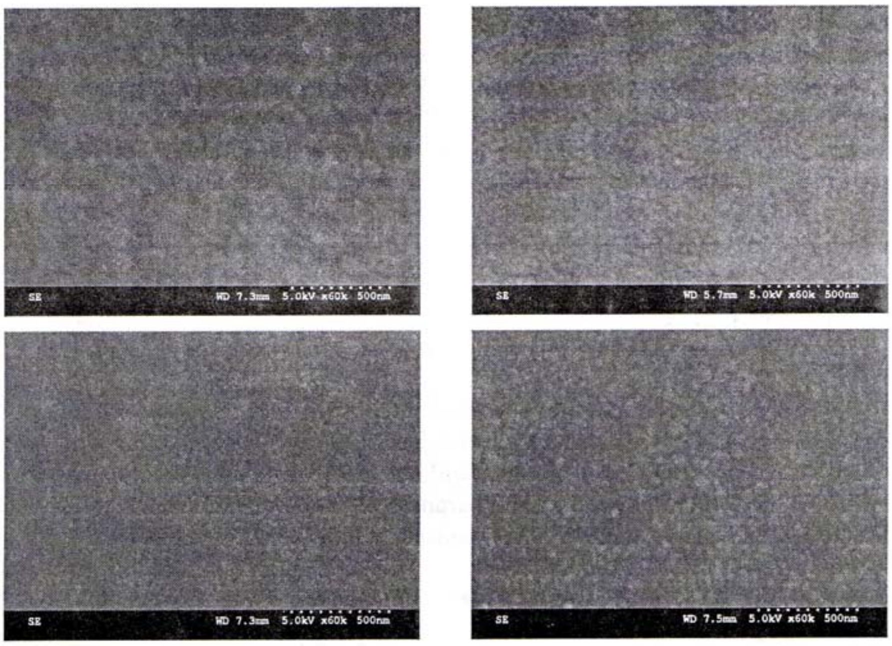

Fig. 3. SEM images of: a) Au, b) Au–0.65% V, c) Au–4.60% V and d) Au–4.00% VO_x thin films deposited on Si wafers after annealing at 200 °C for 1 h

SEM images show general morphologies of the films. After annealing at 200 °C, the Au, Au–0.65% V and Au–4.60% V surfaces (Figs. 3a–c) were composed of a number of nanodots or nanoparticles, although the films did contain a variety of V concentrations. The average size of pure Au particles was 56 nm. The addition of V to Au led to the reduction in their sizes by hindering grain boundary mobility. For the Au–4.00% VO_x surface (Fig. 3d), a number of nanoparticles were also detected. This reflects their properties such as electrical resistivity, surface roughness and hardness.

TEM image data (Fig. 4a) show that the thin film was composed of a number of dispersed, nanosized particles. Different colours (dark, white and gray) appear on the

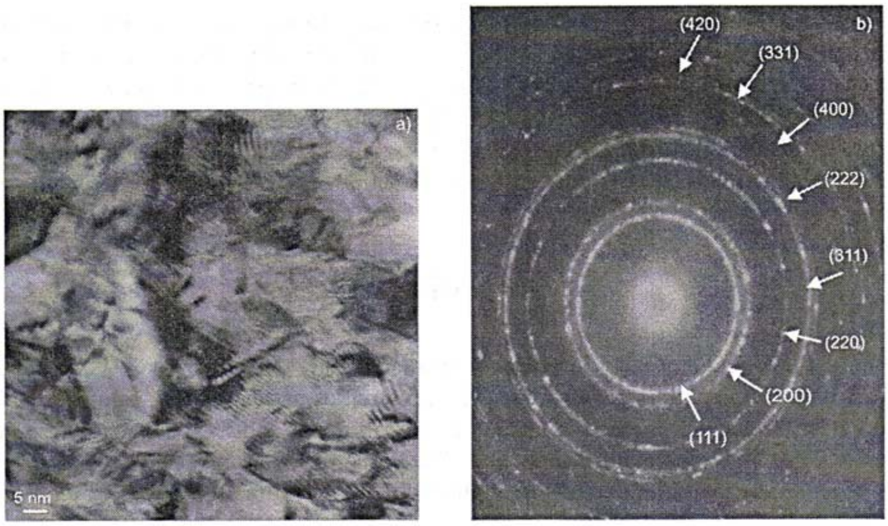

Fig. 4. TEM image (a) and SAED pattern (b) of Au–4.00% VO_x thin film without annealing at a high temperature

image, showing that a rough surface had been produced on the wafer. Moiré fringes were detected. They are the interference patterns of two crystallographic phases with slightly different lattice parameters [14–16]. A SAED pattern (Fig 4b) appears as several concentric rings, due to the diffraction of electrons through the polycrystals. The rings are diffuse and hollow, showing that the thin film was composed of nanosized crystals. Interplanar spaces of the diffraction planes were calculated [17–19] and compared with those computed by the JCPDS software [20]. The pattern corresponds to (111), (200), (220), (311), (222), (400), (331) and (420) planes of the polycrystals, specified as Au (cubic) with *Fm*3*m* space group. The (111) ring has the strongest intensity. No VO_x was detected in the research presented here. Its concentration could have been too low to be detected.

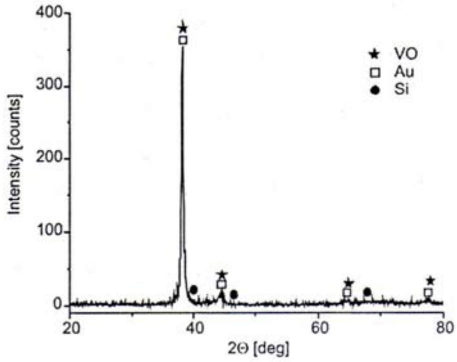

Fig. 5. XRD spectrum of Au–4.00% VO_x thin film deposited on Si wafer without annealing at a high temperature

The XRD spectrum (Fig. 5) was indexed using Bragg's law for diffraction, and was compared with that provided by the JCPDS software [20]. The spectrum is consistent with the deposition of Au and VO_x on Si wafer. It is very sharp, showing that the deposited film was composed of crystals. The strongest intensity peak is at $2\theta = 38.1°$. It mainly diffracted from the (111) plane of Au. VO played a relatively minor role in the diffraction, due to its low concentration (Au–4.00% VO_x).

4. Conclusions

Au, Au–V and Au–VO_x thin films were successfully deposited on Si wafers using a DC magnetron sputtering technique. The resistivities and hardness of thin films deposited on Si wafer increased with the increase in the V and VO_x concentrations decreased after high temperature annealing. The properties were influenced by the number of nanosized particles and different phases of the thin films.

Acknowledgement

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Preparation and characterization of rutile TiO_2 films

Suparut Narksitipan[1,*] and Somchai Thongtem[2]

[1] Division of Materials Science, Faculty of Science, Maejo University, Chiang Mai 50290, Thailand

[2] Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

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

Abstract

Rutile titanium dioxide (TiO_2) films were prepared at calcinations temperature in the range 550-700°C for 4 h prolonged times. Their structure and crystalline are investigated by x-ray diffraction (XRD), selected area electron diffraction (SAED) and raman spectroscopy techniques. After films preparation 700°C, rutile TiO_2 with 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 increasing in the calcinations 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 the surface roughness and the dense particle with angular shape.

Keywords: rutile films, electron microscopy, x-ray diffraction

1. Introduction

Among the numerous oxide materials, titanium dioxide (TiO_2) has received a great 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, pigment for fabrics, dye sensitizer solar cells, and catalyst. TiO_2 has been extensively investigated in recent years because of its many applications such as to purify for air and water from contaminants [1-2], gas sensors [3], and solar cells [4]. TiO_2 as a thin film is able to prepare by various techniques such as sol-gel process [5], chemical vapor deposition [6], evaporation [7] and 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 higher chemical stability, high refractive index, low production cost, etc. For this reason, in the recent years there has been an increasing interest in the preparation and characterization of TiO_2. It was the aim of the present work to investigate the crystalline rutile films, prepared by the thermal oxidation at temperature 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 by 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).

2. Experiment

Rutile films were prepared on the sample (titanium sheet (99.6 % at Ti)) with 1.5 mm thick and cut into 10 mm x 10 mm test coupons. The samples were polished down to 0.3 μm alumina powder and degreased with acetone. They were placed in a furnace, of which the temperature was increased to 550, 600, 650 and 700 °C for 4 h prolong time in air. Finally, the samples were cooled down to room temperature and brought for further characterizations. The structure and crystalline 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°. Raman spectroscopy (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).

3. Results and Discussion

3.1 Structure and crystallinity

After films preparation at calcinations temperature in the range of 550 to 700°C for 4 h prolonged time. Crystallographic planes of XRD spectra are indexed using Bragg's law for x-ray diffraction and compared with those of JCPDS software [9]. XRD patterns of mixture of rutile and oxygen-deficient TiO_2 are shown in Figure 1. XRD pattern of TiO_6 and Ti were detected on the films, which produced between 550 to 600°C and XRD pattern of TiO_6 indicated that the position and intensity of characteristic peaks of the film is well confirmed with JCPDS file No. 72-1807, but amount of TiO6 was quite low. The rutile TiO_2 phase appeared in XRD was confirmed with the JCPDS file No. 04-0551. The characteristic peaks of rutile were evident at 650 to 700°C. The amount of rutile TiO_2 phase increased with increasing 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 Figure 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 the substrate underneath. SAED pattern of the film produced at temperature 700°C are shown in Figure 3. The SAED patterns showed the brightness and intensity of polymorphic discrete ring of crystalline as shown in Figure 3. The diffraction pattern was interpreted and indentified as tetragonal rutile TiO_2. When the films were prepared at high temperature, which showed the intensity of XRD pattern appeared shaper, implied that the higher of crystalline degree of these products. It is worth to note that XRD and SAED analyses are in good accordance. Raman spectra are shown in Figure 4. Rutile film prepared at a temperature of 700°C had strong bands centered at 235, 440 and 603 cm^{-1} wavenumber, which were assigned to be the rutile phase [10]. They were no longer detected at 500°C. The presence of rutile phase characterized by Raman analysis is in good agreement with those characterized by SAED techniques. Therefore, it was concluded that the rutile TiO_2 was prepared at calcinations temperature between 650 to 700°C.

3.2 Morphological analysis

As shown in Figure 4, SEM images of rutile films were prepared at 650 and 700°C for 4 h. They consist of densely particles with angular shape. The particle sizes were in the range of 192 to 252 nm at calcinations temperature between 650 and 700°C. The calcinations temperature was risen, suggests that the crystalline sizes were increased. TEM image of the rutile TiO_2 film produced at temperature 700°C is showed in Figure 5. 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 shown in Figure 6. The roughness values of films were increased from 22.530 to 44.503 nm as the calcinations temperature changed from 550 to 700°C, respectively. The roughness values were increased with increasing in the calcinations temperatures. It is worth to note that the TiO_2 film prepared at 700°C is the most roughness.

4. Conclusions

In conclusion, pure rutile TiO_2 film was successfully prepared at calcinations temperature 700°C for 4 h. When the films were prepared at high temperature, they are higher crystalline and the XRD patterns appeared sharper. The effect of temperature on the films structure was discussed. The SAED and Raman spectra indicated that the film was confirmed to be tetragonal rutile TiO_2 with characteristic structure. The roughness value was increased with increasing the test temperature. At 700°C, the product has the roughest surface - consisting of densely particles and angular surface looks rough.

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.

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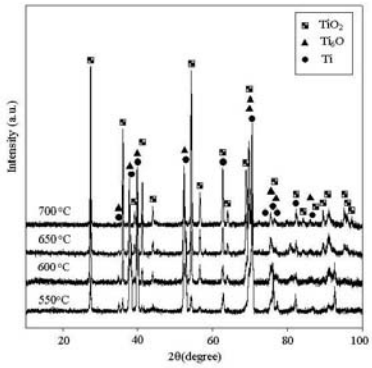

Figure 1 XRD patterns of TiO_2 films produced at different temperatures.

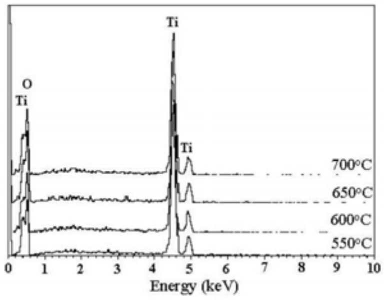

Figure 2 EDX patterns of TiO_2 films produced at different temperatures.

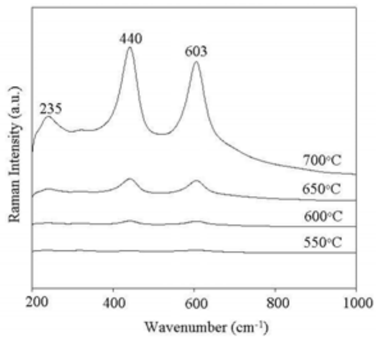

Figure 3 Raman spectra of TiO_2 films produced at different temperatures.

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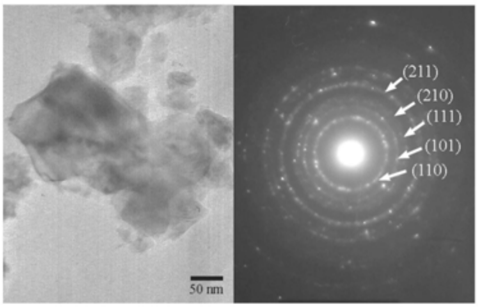
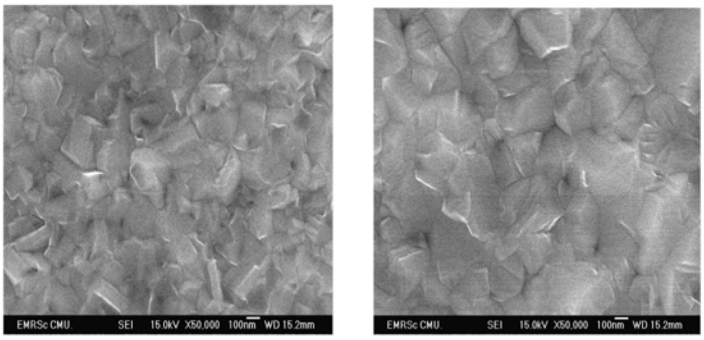
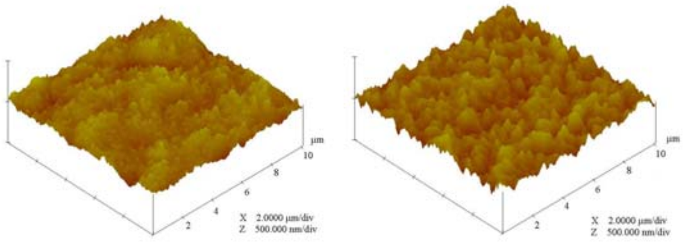


Figure 4 TEM image and SAED patterns of rutile TiO_2 films produced at 700^oC



(a) (b)

Figure 5 SEM images of rutile films produced at (a) 650^oC and (b) 700^oC.



(a) (b)

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

ภาคผนวก ข

การนำเสนอผลงานและตีพิมพ์ผลงานวิจัยใน Proceeding

Dr. Supattra Wongsaennai
Faculty of Science, Maejo University,
Chiang Mai 50290,
Thailand

Dear Dr. Supattra Wongsaennai,

We are pleased to inform you that following two abstracts have been accepted at RCBJSF-10, which will be held in Tokyo Institute of Technology during June 20 to 24, 2010.

"Characterization of Titanium Dioxide Nanoceramics Thin Films"
by Suparut Narksitipan
(Poster presentation, Abstract ID: P1b-22)
"Effect of Li Modified on Phase Formation and Electrical Properties of Potassium Sodium Niobate Ceramics"
by S. Wongsaennai and R. Yimnirun
(Poster presentation, Abstract ID: P1b-23)

Registration for the RCBJSF-10 is now available online at

http://www.msl.titech.ac.jp/~RCBJSF10/index.files/Registration.htm

Guideline for Registration is also posted on the conference website. Please register for the conference at your earliest convenience or before April 1st, 2010 to confirm your participation and to receive the lowest registration rates. At least one author is required to register for the conference for each accepted abstract in order for their papers to be included in the conference abstract book, and to be properly scheduled for the presentation.

The deadline for manuscript submission is June 21th, 2010. The manuscript will be published in "Ferroelectrics" published by Taylor & Francis. The instruction for manuscript preparation has been posted on the conference website.

The complete list of presentations will be available online at

http://www.msl.titech.ac.jp/~RCBJSF10/index.files/Presentations.htm

We look forward to participation at RCBJSF-10. See you in Yokohama, JAPAN

Yours sincerely,
RCBJSF-10 office

Tokyo Instit[illegible]
Materials and Str[illegible]
4259 Nagatsuta, M[illegible], JAPAN

Characterization of Titanium Dioxide Nanoceramics Thin Films

Suparut Narksitipan
Faculty of Science, Maejo University, Chiang Mai 50290, Thailand
E-mail address of author: n_suparut@yahoo.com

Titanium dioxide is widely known to be the best photocatalyst. In this research, titanium dioxide nanoceramics thin films were synthesized by high oxidation temperature in air. The increase in temperature from 300 to 600oC and deposition proceeded for 160 min. The temperature is an important parameter that influences the activity of titanium dioxide thin films. So, the influence of the temperature on the structure properties of titanium dioxide thin films was discussed. X-ray diffraction (XRD), Energy Dispersive X-ray (EDX) used to characterize on the phases composition, crystal structure and elements composition, respective. Deposited thin films morphology was studied by Scanning Electron Microscope (SEM).

After deposition at temperature 600°C, rutile titanium dioxide (TiO_2) phase was detected by XRD as shown in Fig 1. At higher temperature, the oxygen ions have higher energy to react with Ti substrate, titanium dioxide could be formed. However, rutile titanium dioxide phase was not detected below at 600°C treatment temperature. Titanium oxide (TiO_x) phases were detected on the other sample. The phases analyzed by x-ray diffraction were in accord with the elements analyzed by energy dispersive x-ray. The deposited films composed of nanoparticle and quite smooth surface were analyzed by using scanning electron microscope.

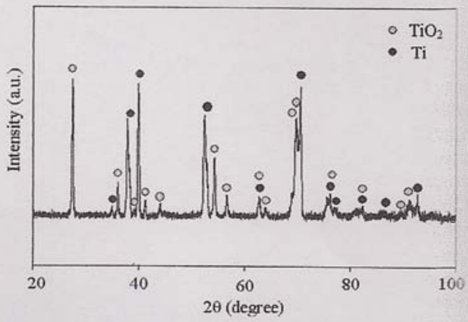
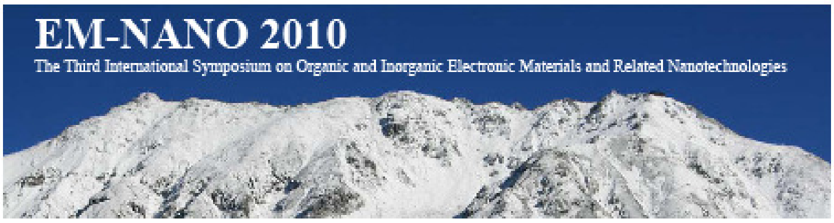


Fig. 1 XRD pattern of rutile titanium dioxide (TiO_2) thin films synthesized at temperature 600°C

Acknowledgements

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



April 7, 2010

Dear Dr. Suparut Narksitipan:

It is our pleasure to inform you that the following paper has been accepted for Oral presentation at EM-NANO2010:

Paper Title: Preparation and characterization of Rutile TiO2 nano thin films
Author(s): Suparut Narksitipan and Somchai Thongtem

Your presentation schedule is as follows:

Paper reference number: 132
Paper presentation number: P1-67
Presentation Date and Time: Wednesday, June 23, 18:00-20:00

We have extended pre-registration deadline to April 28, 2010, so please send registration form to website before the deadline if you have not yet done. For detailed information, please visit the EM-NANO 2010 website http://www3.u-toyama.ac.jp/emnano/index.html.

EM-NANO2010 authors are encouraged to submit original papers on the significant part of their work to be presented at EM-NANO2010 to the Special Issue of Japanese Journal of Applied Physics (JJAP). Submission due date will be scheduled at June 25, 2010. More information about the submission will be announced at EM-NANO 2010 web site.

On behalf of the EM-NANO 2010 organizing committee, we would like to thank you for your participation in EM-NANO 2010, and we are looking forward to seeing you in Toyama, Japan.

Sincerely yours,

Prof. Hiroyuki Okada
Conference chair
Graduate School of Science & Engineering,
University of Toyama
TEL: +81-76-445-6730, FAX: +81-76-445-6732
E-mail: emabst@eng.u-toyama.ac.jp

Preparation and characterization of Rutile TiO_2 nano thin films

Suparut Narksitipan*[,1] and Somchai Thongtem[2]

[1] Faculty of Science, Maejo University, Chiang Mai 50290, Thailand
[2] Department of Physic and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
*e-mail: n_suparut@yahoo.com

Titanium dioxide (TiO_2) has been investigated extensively in recent years because of its many applications, such as gas sensors, photocatalysis, and dry-sensitization for solar cells [1-3]. In this research, nanocrystalline rutile thin films were prepared at temperature in the range 550-700°C for 4 h prolonged times. Their structure was investigated by X-ray diffraction (XRD) and Raman spectroscopy. The XRD investigations showed that the films deposition at temperature higher than 600°C composed of tetragonal rutile TiO_2 and TiO_6, as referred in the JCPDS 04-0551 and 07-1807 files, respectively, as shown in Fig. 1. Additional Ti spectrum was detected on the film deposition at temperature below 600°C, which indicated that the X-ray beam penetrated the deposition layer. Raman spectra of the deposition films were preformed in the range of 100-1000 cm^{-1}. The Raman spectra displayed band at 235, 439 and 603 cm^{-1} correspond to the rutile structure of TiO_2. The intensity of rutile TiO_2 was increased with increasing in the temperature, which implying that the films with higher rutile structure. The Raman spectra agree very well with rutile spectrum of XRD results, which previously investigated. In Fig. 2, a typical SEM micrograph of TiO_2 films was prepared at temperature 700°C. The rutile films were grown densely. However, the surface was rough and facets were observed.

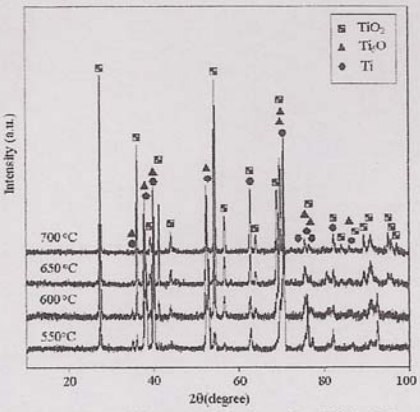


Fig. 1 XRD spectra of rutile TiO_2 thin films at temperature in the range 550-700°C for 4 hour proceed time

Fig. 2 Typical SEM micrograph of rutile TiO_2 thin films at temperature 700°C

Acknowledgements

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

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Chulalongkorn University, Phya Thai Rd., Bangkok 10330
Tel: 085-018-3131, 02-2527987, 02-2185245 Fax. 02-2527987
E-mail: s_srisung@hotmail.com, kkung.scisoc@gmail.com, jaksriri14@hotmail.com

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รศ.ดร. ธาราวัตน์ ศุภศิริ

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Keywords: rutile, titanium dioxide (TiO_2), Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM)

อิทธิพลของอุณหภูมิต่อองค์ประกอบเฟสของฟิล์มไทเทเนียมไดออกไซด์

The influence of temperature on the phase compositions of titanium dioxide films

ศุภรัตน์ นาคสิทธิพันธุ์*

Suparut Narksitipan*

Division of Materials Science, Faculty of Science, Maejo University, Chiangmai, Thailand
*e-mail: n_suparut@yahoo.com

บทคัดย่อ:
ฟิล์มไทเทเนียมไดออกไซด์ถูกเตรียมในช่วงอุณหภูมิ 300 ถึง 600 องศาเซลเซียส เป็นเวลา 160 นาที แล้วทำการวิเคราะห์ฟิล์มดังกล่าวด้วยเทคนิคการเลี้ยวเบนด้วยแสง (XRD) เพื่อศึกษาองค์ประกอบของเฟส และโครงสร้างผลึกของฟิล์ม เทคนิคการวิเคราะห์ธาตุด้วยรังสีเอกซ์ (EDS) เพื่อศึกษาองค์ประกอบธาตุบนฟิล์ม ศึกษาลักษณะทางสัณฐานวิทยาและความหยาบของพื้นผิวของฟิล์มด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) และกล้องจุลทรรศน์แบบอะตอมมิกฟอร์ซ (AFM) ตามลำดับ พบเฟสของรูไทล์โครงสร้างแบบเตตระโกนอล ที่ช่วงอุณหภูมิของการสังเคราะห์ 500 ถึง 600 องศาเซลเซียส และปริมาณของเฟสรูไทล์เพิ่มขึ้นเมื่ออุณหภูมิในการสังเคราะห์เพิ่มสูงขึ้น ซึ่งสอดคล้องกับผลการวิเคราะห์ด้วยเทคนิค EDS ศึกษาลักษณะทางสัณฐานวิทยาของฟิล์มด้วย SEM พบว่า ฟิล์มดังกล่าวประกอบด้วยอนุภาคที่มีรูปร่างไม่แน่นอนและอนุภาคค่อนข้างหนาแน่น ผิวของฟิล์มที่ได้ค่อนข้างหยาบจากการตรวจสอบด้วย AFM

Abstract:
Titanium dioxide (TiO_2) films were prepared at the temperature in the range 300 to 600°C in air for 160 min prolonged time. So, the influence of the temperature on the structure of titanium dioxide thin films was discussed. Phase compositions and crystal structure were characterized by using XRD technique. EDS were analyzed element compositions on the films. Moreover, films morphology and roughness were studied by SEM and AFM techniques, respectively. It was found that the rutile phase with tetragonal structure at calcinations temperature in the range 500 to 600°C, which detected by XRD. The intensity of rutile TiO_2 increased with increasing calcinations temperature. The phases analyzed by XRD were in accord with the elements analyzed by EDS. The films composed of particle with angular shape and rough surface, which analyzed by SEM and AFM.

Introduction: Titanium dioxide (TiO_2) is widely known to be the best photocatalyst. The temperature is an important parameter that influences the activity of titanium dioxide thin films. TiO_2 is commonly used as coating materials in optical thin films because it is highly transparent and has high refractive index and chemical durability in the visible and near-infrared regions of the spectrum [1]. TiO_2 has attracted considerable attention because of its wide range of applications in the optical filter, photocatalytic, and gas sensing fields [2-4]. TiO_2 as a thin film is able to prepare by various techniques such as sol-gel process [5], chemical vapor deposition [6], evaporation [7] and sputtering method [8]. In general, crystalline TiO_2 film exists in three phases: anatase (tetragonal), brookite (orthorhombic) and rutile (tetragonal) [9-10]. Rutile being the most stable of the three, and the formation of its phase depends on starting materials, deposition method and calcinations temperature. In particular, TiO_2 thin films can transform from amorphous phase into rutile by calcinations. Therefore, it is necessary to study the effect of calcinations temperature on phase of TiO_2 thin films. The purpose of this research was to study of the influence of temperature on the phase compositions of TiO_2 films. Therefore, TiO_2 thin films were prepared at temperature in the range 300-600°C in air for 160 min. TiO_2 thin films were characterized using XRD, EDS, SEM and AFM techniques. And the influence of temperature on the phase and morphology of prepared TiO_2 thin films was investigated.

Methodology: Rutile titanium dioxide (TiO_2) thin films were prepared on the titanium sheet (99.6 % at Ti) with 1.5 mm thick and cut into 10 mm x 10 mm test coupons. The samples were polished down to 0.3 μm alumina powder and degreased with acetone. They were placed in a furnace, of which the temperature was increased to 300, 400, 500 and 600 °C for 160 min prolong time in air. Finally, the samples were cooled down to room temperature and brought for further characterizations. The structure and crystalline 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 morphological characterization of the films was performed by means of scanning electron microscopy (FE-SEM JSM-6335F) and atomic force microscopy (Nano Scope ® IIIa by Veeco Digital Instrument).

Results, Discussion and Conclusion: Figure 1 illustrates the XRD patterns of TiO_2 thin films were prepared at various temperatures from 300 to 600°C for 160 min in air. The XRD results showed that the titanium spectra, which indicated the X-ray beam penetrated the film, reflected the substrate underneath and refracted from the films layer. Rutile titanium dioxide (TiO_2) phase was detected at temperature 500 and 600°C, which corresponding with JCPDS number 04-0551 [10]. The strongest intensity is at $2\theta = 27.46°$, belonging to tetragonal rutile (110) plane of crystalline product. The intensities of rutile peaks were increased when the temperature increased from 500 to 600°C, which agree with Ref [9]. Figure 1, peaks in the XRD patterns become sharper, indicated that the rutile TiO_2 films were further crystallized. EDS patterns as shown in Figure 2, titanium (Ti) and oxygen (O) spectra were detected at various temperatures from 300 to 600°C. Moreover, the intensities of oxygen increased with increasing temperature. So, EDS results confirmed that the formation of rutile TiO_2 in these films.

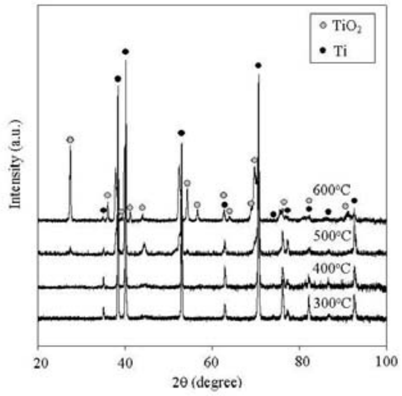

Figure 1. XRD patterns of thin films prepared at various temperatures for 160 min.

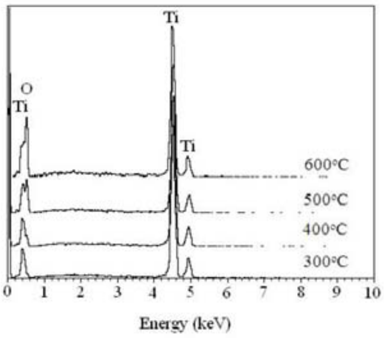

Figure 2. EDS patterns of thin films prepared at various temperatures for 160 min.

The morphologies of thin films were characterized by SEM and AFM techniques are shown in the Figure 3 and Figure 4, respectively. SEM micrograph revealed that the rutile TiO_2 film surface consisted particles with angular shape and densely. The effect of temperature, which was increased to 600^{o}C, the film was grown and shifted into the agglomerate state. Therefore, the surface of films was quite rough. The roughness on the surface was measured by AFM technique. The roughness value was increased with increasing temperature. The value at 600^{o}C was 61.709 nm. It was found that the film prepared at 600^{o}C is the most roughness.

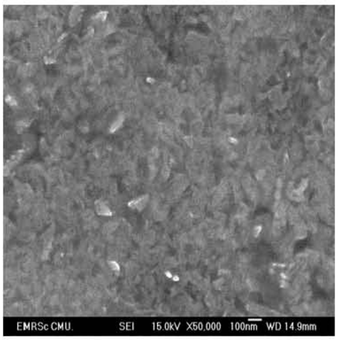

Figure 3. SEM micrograph of thin film prepared at temperature 600°C for 160 min.

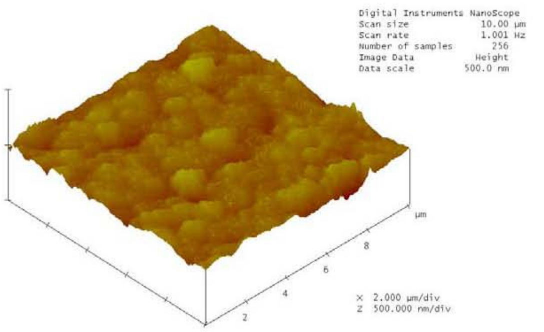

Figure 4. AFM micrograph of thin films prepared at temperature 600°C for 160 min.

In conclusion, tetragonal rutile TiO_2 film was successfully prepared at temperature in the range of 500 to 600°C. The intensities of rutile phase was increased with increasing in the temperature, as well as, the films are higher crystalline. At temperature 600°C, the film has the roughest surface and composed of densely particle with angular shape. The size value of particle was less than 100 nm.

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Influence of Oxygen Ions on the Structure of Titanium Oxide (TiO_x) Thin Films Prepared by Plasma Deposition Technique

Suparut Narksitipan[1]
[1] Materials Science, Faculty of Science, Maejo University, Chiang Mai 50290, Thailand
*Corresponding author, e-mail: n_suparut@yahoo.com

Abstract

Titanium oxide (TiO_x) thin films have been prepared by using plasma immersion ion implantation and deposition (PIIID) technique in oxygen atmosphere was used as a source for oxygen ions, which was deposited onto the titanium surface. Before deposition the chamber was pumped to a base pressure below $2x10^{-5}$ Torr. The argon gas was fed into the chamber to $1.5x10^{-3}$ Torr. A radio frequency (RF) generator discharges at 13.56 MHz and 150 W. The -2.5 kV bias voltage was supplied for 10 min to clean the titanium surface and turn off. Then, the argon was evacuated to 10^{-5} Torr and oxygen gas was fed into the chamber. This results in a working pressure of $2x10^{-3}$ Torr and transferred into oxygen plasma by RF glow discharge at 250 W. The -20 kV bias voltage was supplied and increase the ions density of $3.0\ x10^{-7}$- $6x10^{-7}$ ions/cm^2 to prepare the TiO_x thin films. The influences of ion density on the structure properties of TiO_x thin films were investigated. Films deposited phases were analyzed using X-ray diffractometer (XRD) and the Kα line from a Cu target in combination with JCPDS software [1]. The phases of TiO_2, TiO and TiO_6 were detected on the surface, which ions density more than as shown in figure 1. During oxygen plasma deposition, titanium reacted with oxygen lead to form TiO_x. The strong diffraction peaks were form the (011) rutile TiO_2 and (101) TiO at 2θ approximately of 40° and 44°, respectively. The intensity of TiO_2 peak shows slight increase with increasing of the oxygen ion densities. The detection of Ti shows that the x-ray beam penetrated the deposited layer and was refracted from the underlying alloy matrix as well as the deposited layer. Figure 2 revealed EDX results of Ti and O spectra on the deposited films at ions density of 6.0×10^{-7} ions/cm^2. Ti and O spectra generates from TiO_x in the deposited layer. The EDX results confirmed with the phase compositions, which were analyzed by XRD. A scanning electron microscopy image indicates that the films composed of nano-particles and smooth surface as shown in figure 3.

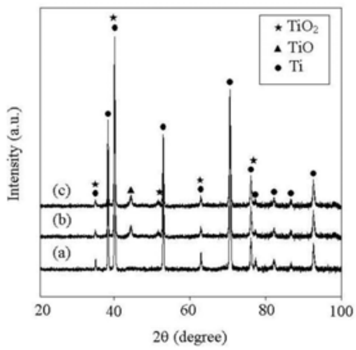

Figure 1 XRD patterns of deposited films with the oxygen ion densities of (a) 3.0×10^{-7} ions/cm^2, (b) 4.5×10^{-7} ions/cm^2 and (c) 6.0×10^{-7} ions/cm^2

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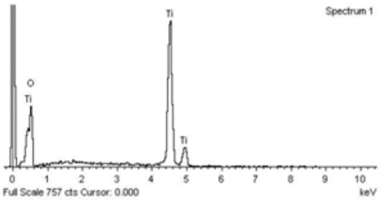

Figure 2 EDX spectra of the deposited film with oxygen ion density of 6 x 10^{-7} ions / cm^2

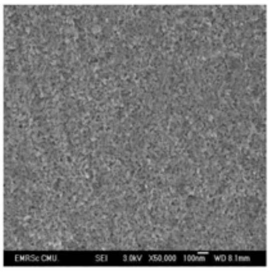

Figure 2 SEM image of the deposited film surface with oxygen ion density of 6 x 10^{-7} ions / cm^2

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