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Microstructure Evolution of Ag/TiO_2 Thin Film

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Abstract: Ag/TiO_2 thin films were prepared using the sol-gel spin coating method. The microstructural growth behaviors of the prepared Ag/TiO_2 thin films were elucidated using real-time synchrotron radiation imaging, its structure determined using grazing incidence X-ray diffraction (GIXRD), its morphology imaged using the field emission scanning electron microscopy (FESEM), and its surface topography examined using the atomic force microscope (AFM) in contact mode. The cubical shape were detected, identified as Ag, while the anatase, TiO_2 thin film resembles a porous ring-like structure. It was found that each ring coalescing and forming channels occurred at low annealing temperature of 280 ˚C. The growth rate of Ag/TiO_2 is 47.26 $\mu m^2/s$ at early 600 s and continued grown at a slow rate of 11.50 $\mu m^2/s$ at 1200 s before the growth rate was slowly increased to 11.55 $\mu m^2/s$ at 1800 s. Then the rate was slow down at 2400 s, 3000 s and 3600 s, respectively. It was revealed that the junction growth orientations and patterns were grown randomly.

Keywords: Microstructure; Titanium Dioxide; Thin Film; Sol-Gel; Synchrotron Radiation Imaging

1. Introduction

Titanium dioxide (TiO_2) has been widely used as a photocatalyst especially in the field of energy and environmental applications due to its chemical stability and excellent physical, optical, electrical, and photoelectrochemical properties. The TiO_2 also has a good optical transparency in the visible and near-infrared (IR) regions with high refractive index [1-3]. In addition, its strong oxidizing ability vis-a-vis organic pollutants, superhydrophilicity, durability, non-toxicity and cost-effectiveness, making it an effective photocatalyst [4-5]. TiO_2 has three different crystalline phases namely anatase, rutile, and brookite. It is found that the anatase phase is actively photocatalytic compared to the rutile phase. This can be attributed to the larger bandgap in the anatase phase that can increase both the charge carrier lifetime and also the surface redox potential. The photocatalytic activity of TiO_2 thin films does not depend only on the phase but also, on the crystallite size and porosity [6-8]. Besides that, the grain size, specific surface area, pore volume and structure, and microstructural growth are some of the factors which can influence the photocatalytic performance of TiO_2 thin films.

The properties of the TiO_2 thin films depend on the preparation technique and deposition parameters. In the sol-gel synthesis, thin films' formation relies on parameters such as the sol's

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reactivity, viscosity, water alkoxide ratio, and metal precursor concentrations [9]. TiO_2 thin film nanostructures have a large surface area and exhibit unique physicochemical and electronic properties that differ from their bulk counterpart [10]. Yin et al. outlined the morphological conditions and growth of pure TiO_2 thin film via a cross-sectional display of a TiO_2 monolayer thin film [11].

The addition of dopants in TiO_2 thin films affects its surface morphology and roughness [12]. Sajid et al. posited that the addition of 0.75% Ag in TiO_2 resulted in a thermally-stable TiO_2 anatase phase with small particle size and uniform morphology, high surface area, and low excitation energies. Ag/TiO_2 samples with 0.75% Ag also had well-distributed Ag species (Ag_2O and AgO) across its surface [13]. The percentage of Ag agglomerates on the surface (AgO) increases as the Ag content in the Ag/TiO_2 sample increases [14]. The majority of microstructural studies are conducted using only SEM and are limited to observations of the films' surface morphology and thicknesses. Some studies used AFM to analyze the films' surface topography, but they are somewhat limited in number.

The growth process of films can be described by the phase transformation from anatase to rutile, which can be affected by the grain boundary concentrations, particle packing factors and the defects existed in the microstructure [15-16]. Controlled on the phase structure of the films during growth is critical as the properties of TiO_2 films are highly dependent on the crystal structures, morphologies and orientations. Most study suggested that the sol-gel process is highly favorable due to its advantages that include low-temperature and low-cost process, controllable film morphologies and composition and the possibility to be coated on a large-area. The synthesis of sol-gel deposited TiO_2 thin films' can be manipulated by altering the processing conditions that include the choice of solvents, solvent concentrations, and post-deposition annealing temperatures [17]. Previous work on TiO_2 film, annealed at 400–700 °C, showed a predominantly anatase phase structure and by controlling the Ag molar ratio, it was found that the Ag nanoparticles was uniformly distributed and strongly attached to the mesoporous TiO_2 matrix [18-19]. This work aims to study Ag/TiO_2 thin films' microstructural evolution during annealing at a low annealing temperature of 280 °C.

2. Materials and Methods

2.1 Materials

Titanium (IV) isopropoxide 97% (TTIP) was used as a precursor, and silver nitrate ($AgNO_3$) powder was used as the source of Ag. Both were purchased from Sigma Aldrich. Propan-2-ol was purchased from QReC Chemicals, while acetic acid (99.5%) and methylene blue (MB) were purchased from Daejung Reagent Chemicals. The chemicals were of analytical reagent grades and used as received without further purification. The hydrolysis reaction will result in precipitation using precursors with strong reactivity towards water (titanium alkoxide). The non-aqueous sol-gel technique was used with titanium chloride or titanium alkoxides as a precursor to mitigate the precipitation.

2.2 Preparations of Ag/TiO_2 Thin Film

To prepare the Ti precursor sol, a given TTIP volume was dissolved in 20 ml isopropanol. The solution was then stirred continuously for 10 mins at room temperature. This if followed by the dropwise addition of mixed solution of 0.1 ml water, 2.0 ml ethanol, and 0.1 ml of 0.1 M $AgNO_3$ while stirring the solution for another 10 mins. A small aliquot of concentrated acetic acid of a negligible dilution was then added to adjust the solution. The produced alkoxide solution was stirred until a transparent sol was formed without any precipitation. To deposit the thin film, glass substrates (15 mm×15 mm×0. 5 mm) were used. The substrates were degreased and cleaned with acetone for 30 mins in an ultrasonic cleaner and thoroughly rinsed with water. The substrates were then dried at 90 ◦C for 90 mins in lidded Petri dishes and then stored for further use. To prepare the Ag/TiO_2 thin films, the Ti precursor sol was dropped on the substrate and spin coated at 500 rpm for 10 s, followed by 2000 rpm for another 30 s. The sample was then dried on a hotplate at 60 ◦C for 10 mins.

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2.3 Characterizations

The prepared Ag/TiO_2 thin films were characterized using the GIXRD at 0°- 80° with a Cu Kα (λ=1.5046). The GIXRD patterns were identified using the Diffract Eva Software. The films' morphologies were imaged using a FESEM, its surface topography examined using an AFM in contact mode, and the growth behavior elucidated the real-time synchrotron radiation imaging technology. A real-time observation was performed at the BL20XU beamline in the Spring-8 synchrotron using the imaging observation setup. The nucleation and growth of microstructure and the formation of thin-film were observed using synchrotron. A camera with a resolution ratio of 2.74 μm per pixel and an exposure time of 1 s/frame was used to capture images of the growth process of the Ag/TiO_2 thin films, while X-ray energy of 21 KeV between the edges was used to create a higher contrast between the primary and secondary phases. The samples' position and cell configuration are shown in **Figure 1.** The observation window area of 10 × 10 mm with a vent for flux outgassing was made using a 100 μm thick polytetrafluoroethylene (PTFE) sheet placed between two SiO_2 plates. The sample was annealed from room temperature to 280 °C at 0.33 °C/s and held for an hour before cooling at a rate of ~0.33 °C/s.

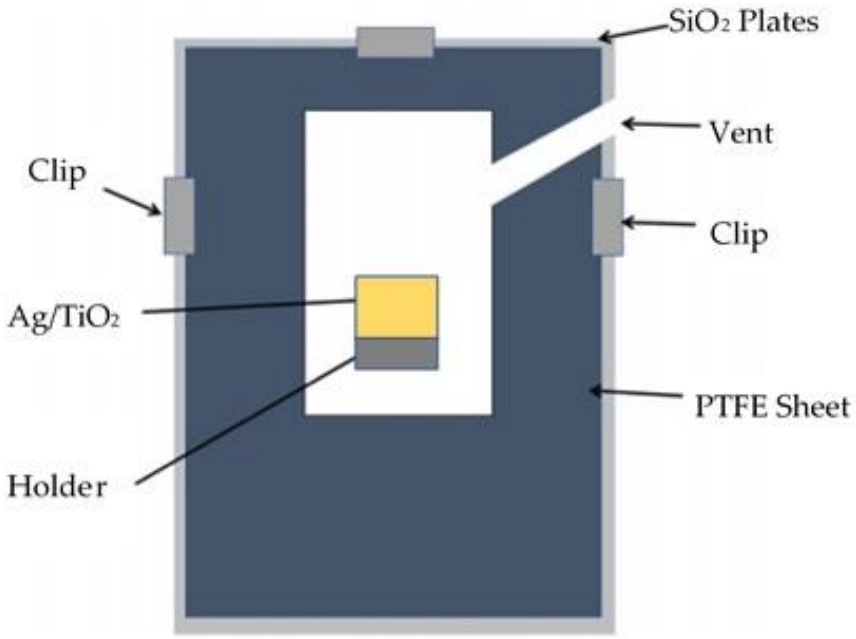

Figure 1. The schematic diagram setup of the real-time synchrotron radiation imaging

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3. Results and discussion

3.1 Phase composition

The Ag/TiO_2 thin films were analyzed using the GIXRD, and the results are shown in **Figure 2.** The GIXRD pattern revealed characteristic peaks at 2θ of 24.8°, 37.3°, 47.6°, 55.1° and 62.2°, which represent different crystallographic planes corresponding to the anatase phase of TiO_2, (101), (004), (200), (211) and (204), respectively (JCPDS Card No.: 21-1272). The diffraction peak of Ag is seen at 38.2^0, 44.4^0 and 64.6^0 at crystal plane (111), (220) and (220), matched with JCPDS card of Ag (No.04-0783) [20], in line with Akgun & Duruchan, who reported that the addition of small amounts of Ag into TiO_2 thin films resulted in the presence of anatase and rutile phases along with two extra peaks of Ag at 38.2° and 44.4° [21]. It can also be seen that additional GIXRD peaks that correspond to the Ag area are clearly defined in the pattern.

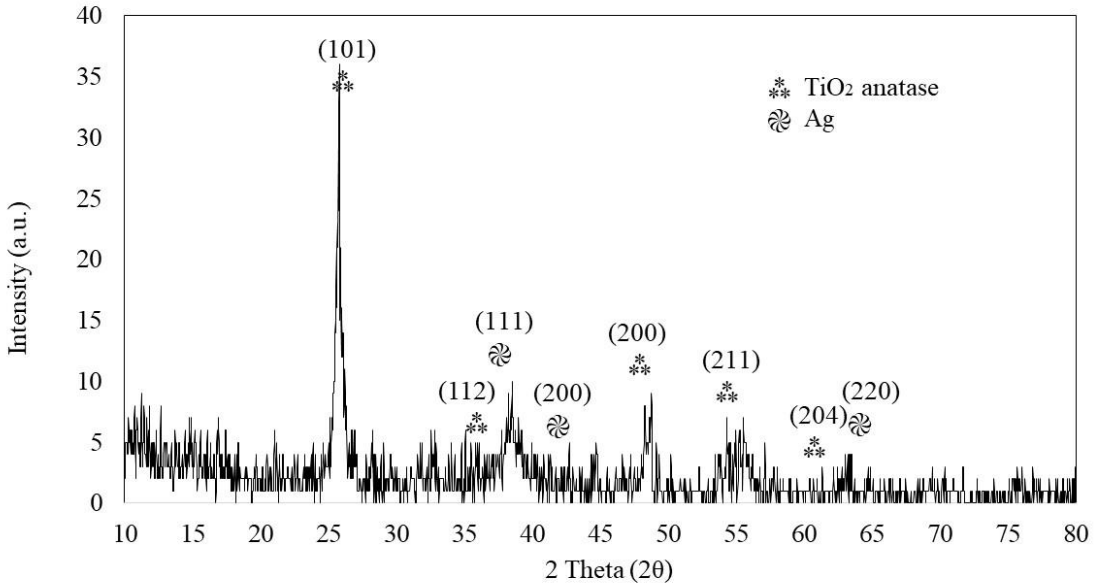

Figure 2. The GIXRD pattern of Ag/TiO_2 thin film

3.2 Microstructural and topography analysis

The samples were imaged using FESEM and AFM to elucidate the nature of Ag's incorporation into the TiO_2 film (doping/segregation). The surface microstructure of Ag/TiO_2 thin films obtained from the FESEM micrographs are shown in **Figure 3**. Theoretically, there are several stages for the films' formation, which are (1) the nucleation stage, encompassing the condensation of vapors, adsorption of atoms, migration of atoms, formation of critical nuclei and stable clusters; (2) the films forming an island structure; (3) the coalescence of the island with gaps in between; (4) the channel stage; (5) the formation of a continuous film [22]. The Ag particle deposits distributed randomly on the surface of TiO_2 thin film are evident in **Figure 3**(a), which is still in the third or fourth stage of its growth. The Ag particle mostly in cubical shape, while the TiO_2 thin film resembles porous ring-like structures, where each ring coalescences to form a channel of ring. Due to the low annealing temperature, the porous ring-like structures lack the energy to form continuous films. The structures limit the pore accessibility in the thin films, as the interfacial energy between the substrate's surface and the films often leads to the pores positioned parallel to the substrate surface [23]. **Figure 3** (a) shows the distribution of Ag on the surface of TiO_2 thin films, and it is evident that Ag precipitation

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is represented on the TiO_2 thin film with the Ag's average particle size estimated ~ 0.1 μm. The presence of Ag also confirms the ability to form it on TiO_2 thin film at low temperatures. It can be concluded that the coalescences of porous ring-like structures for TiO_2 thin film and the formation of cubical shape of Ag can be occurred at low temperature of 280 ˚C.

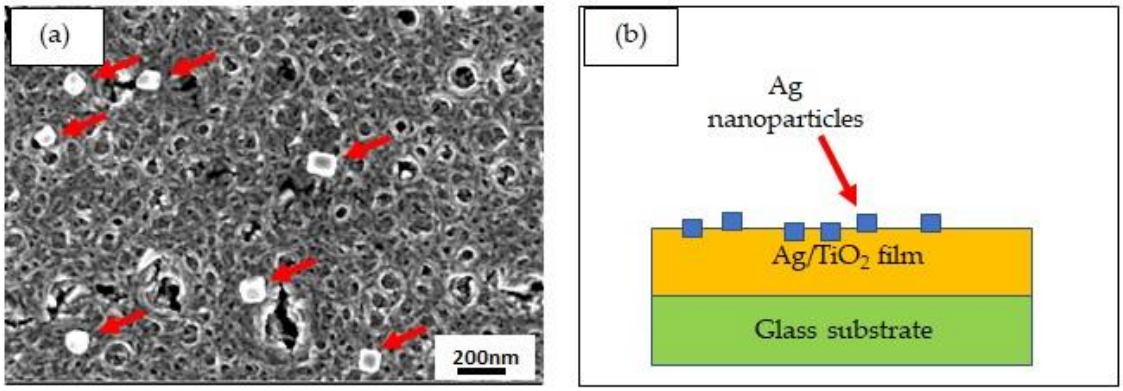

Figure 3. Microstructural FESEM micrographs of (a) Distribution of Ag particles onto TiO_2 thin film; (b) schematic diagram of Ag particles formed on TiO_2 layer which was deposited onto a glass substrate.

Figure 4 shows the AFM topography of the Ag/TiO_2 thin film. The root mean square (RMS) roughness values obtained from the AFM for these films is 10.52 x 10^{-3} μm, at a thickness of ~83.72 x 10^{-3} μm. The thin film's surface's roughness can be attributed to two factors; limited surface diffusion caused by relatively low thermal energy and a crystallite size effect. It is believed that during grain growth, anatase phase is dominant due to its lower surface energy and higher driving force forming a high volume to surface ratio grains. However, at higher temperatures, voids are formed and thus repositioned the existing anatase grains into the lower surface areas before transforming them into rutile. The lower surface energy of the anatase grains subsequently affects its growth, making the rutile phase more apparent in the structure [24]. Kumar et al. reported Ag/TiO_2 nanocomposite films' synthesis via the sol-gel method followed by electron beam physical vapor deposition (PVD). The RMS value of their films was in a good agreement with the RMS value of the films obtained in this work [25].

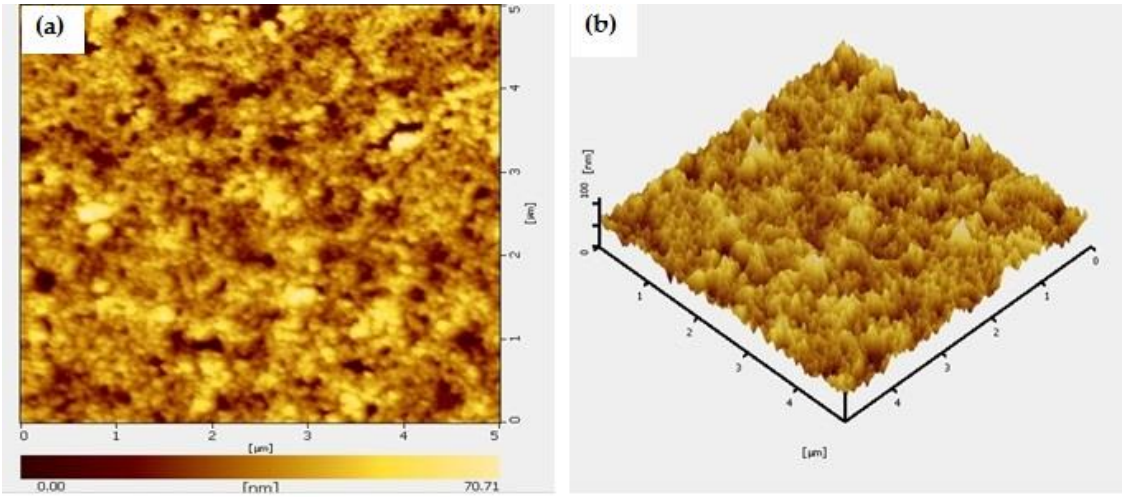

Figure 4. Surface topographical profile of Ag/TiO_2 thin film

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3.3 *Growth behavior of Ag/TiO₂*

The growth behavior of the Ag/TiO_2 was elucidated using in-situ synchrotron radiation imaging technology. As per **Figure 5**, it can be seen that the growth of junctions is increase with increases of time when annealed at 280 ˚C. The phase of Ag/TiO_2 grown from 600 s to 3600 s, as shown in **Figure 6** (a-g), making the growth measurable. Image-J software was used to calculate the area of Ag/TiO_2. The investigation on the growth of Ag/TiO_2 was conducted as shown in **Figure 6 (a-f)**. The white area is the Ag/TiO_2 and black area is glass substrate. The area began increasing from 28359 μm² at 600 s to 35263 μm² at 1200 s. This area continues to grow with increased annealing time, to 42198 μm² at 1800 s, 45764 μm² at 2400 s, 48241 μm² at 3000 s, and 51161 μm² at 3600 s as shown in Figure 6(g). From the result we can calculate the growth rate of this Ag/TiO_2 phase. At 600 s, the growth rate of Ag/TiO_2 is 47.26 μm²/s and continued grown at a rate of 11.50 μm²/s at 1200 s before the growth rate was slowly increased to 11.55 μm²/s at 1800 s. Then the growth rate started to slow down for 2400 s, 3000 s and 3600 s at 5.94 μm²/s, 4.12 μm²/s and 4.86 μm²/s, respectively. This observation implies that the area of Ag/TiO_2 growth when annealed at low temperature 280 ˚C. During the annealing at 280 ˚C, the phase of Ag/TiO_2 growth without no cracks were detected.

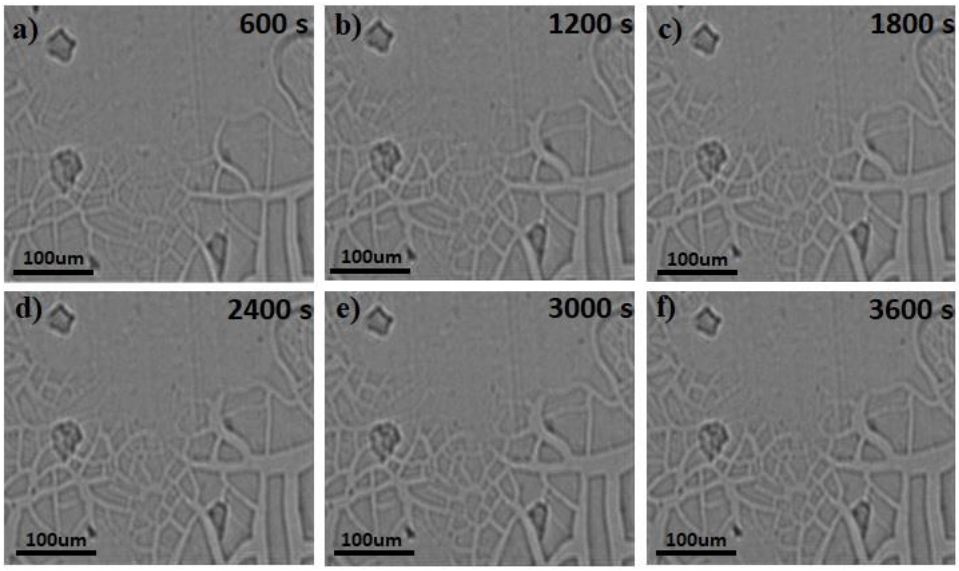

Figure 5. The growth behavior of Ag/TiO_2 thin film for (a) 600 s, (b) 1200 s, (c) 1800 s, (d) 2400 s, (e) 3000 s, and (f) 3600 s at 280 ˚C.

The junctions of Ag/TiO_2 were also measured, and the results are shown in **Figure 7**. This junction refers to the how easily the junction form at 280 ˚C. The white area shows the phase of Ag/TiO_2 form during the annealing process. It shown that the junction at 600 s is 32; it continuously increases with time to 67 junctions at 1200 s, 70 junctions at 1800 s, 72 junctions at 2400 s, 76 junctions at 3000 s, and 78 junctions at 3600 s of annealing time. These observations confirm that the growth of the junctions of the Ag/TiO_2 phase is increases with the time. The junctions grown at random orientations and patterns. This junction also can be related with the morphology of Ag/TiO_2. The TiO_2 thin film resembles porous ring-like structures and this porous ring-like structures lack the energy to form a continuous film. The surface roughness also can be attributed to the quantity of the junctions.

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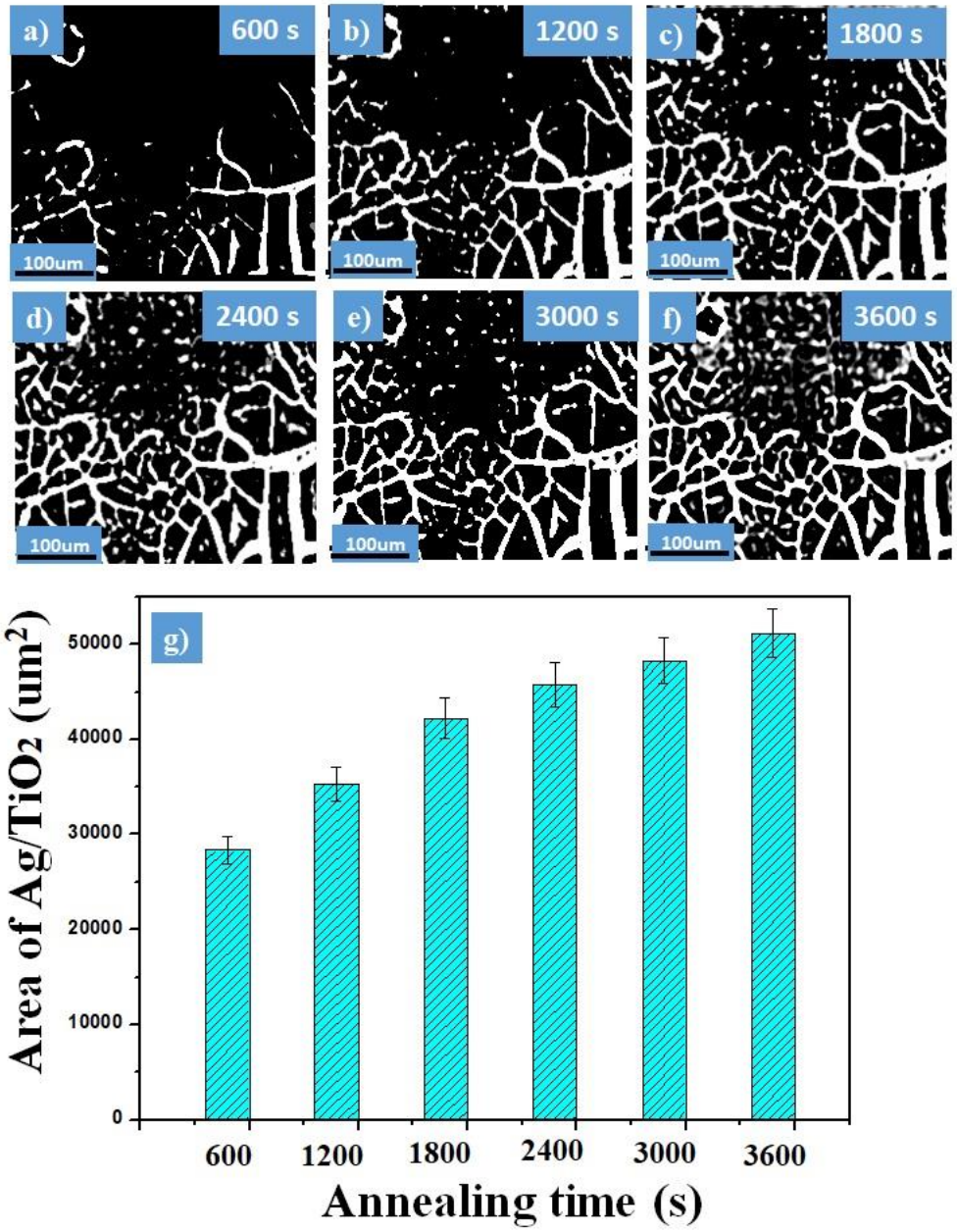

Figure 6. Growth of Ag/TiO_2 area during the annealing time at (a) 600 s, (b) 1200 s, (c) 1800 s, (d) 2400, (e) 3000 s, (f) 3600 s and (g) graph of area Ag/TiO_2 versus annealing time.

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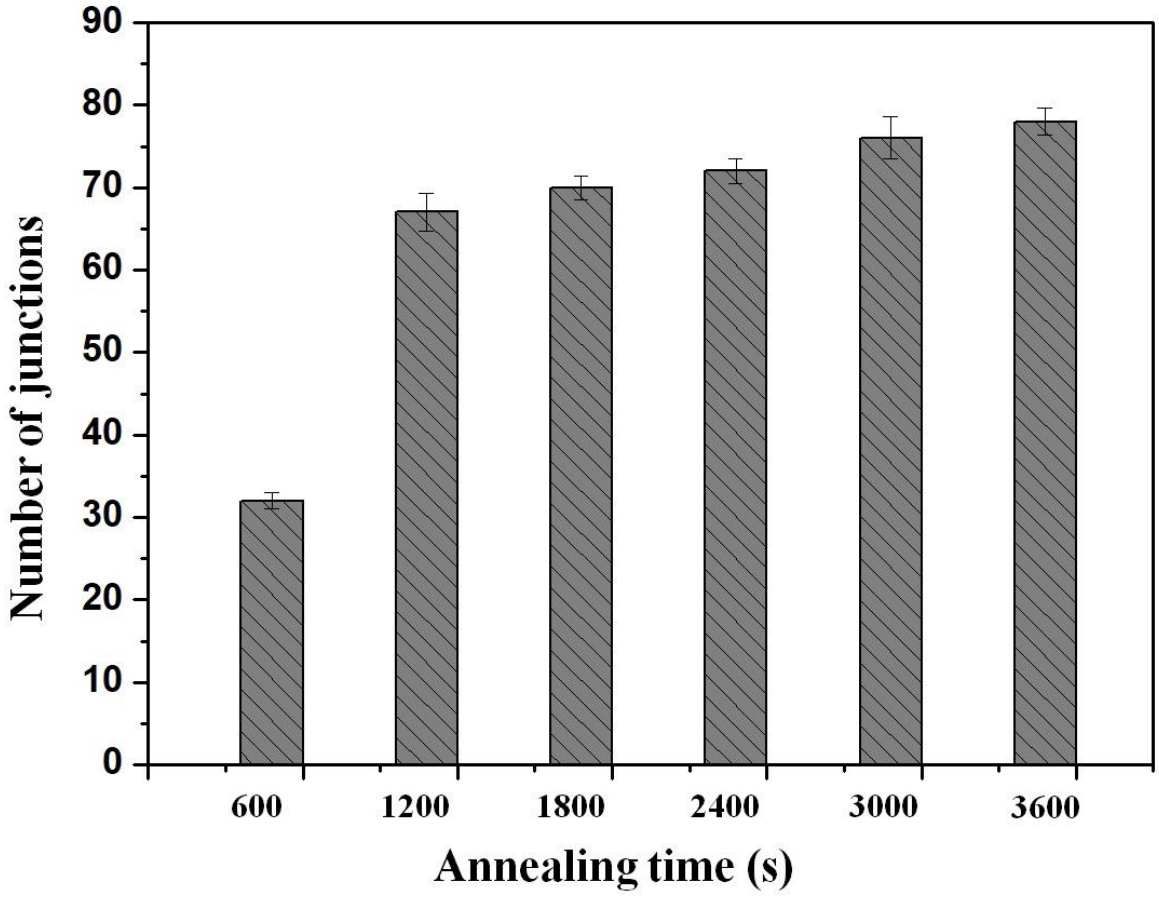

Figure 7. The numbers of junction formation during the different annealing time (s)

4. Conclusions

This work was successfully synthesizing Ag/TiO_2 thin films onto a glass substrate via the sol-gel spin coating method. The deposited films were annealed at a low temperature of 280 °C and analyzed using a beamline in the Spring-8 synchrotron with the imaging observation setup. It was found that the obtained Ag/TiO_2 thin film was suitable to be used as photocatalyst especially in the field of energy and environmental applications. The growth evolution of the microstructure and the formation of the thin films were successfully observed. The results show that:

(a) The GIXRD pattern was confirmed that the anatase phase with the diffraction peak of Ag can be seen clearly even at low annealing temperature.

(b) The FESEM micrograph confirmed the Ag particles were mostly cubical, while the TiO_2 thin film resembled porous ring-like structures, where each ring coalesces to form a channel of ring. It was revealed that the coalescences of porous ring-like structures for TiO_2 thin film and the formation of cubical shape of Ag can be obtained at low annealing temperature.

(c) The surface topographical profile shows the root mean square (RMS) roughness values obtained by the AFM for the film is 10.52 x 10^{-3} μm with a thickness of 83.72 x 10^{-3} μm. The film's surface was rough due to the limited surface diffusion caused by the relatively low thermal energy and the crystallite size effect.

(d) The real-time synchrotron radiation imaging technology was used to elucidate the Ag/TiO_2 thin film's growth behavior films. The growth start with 47.26 $\mu m^2/s$ at early 600 s and then grown at 11.50 $\mu m^2/s$ at 200 s and 11.55 $\mu m^2/s$ at 1800 s then were slowly down at 5.94 $\mu m^2/s$, 4.12 $\mu m^2/s$ and

4.86 μm²/s for 2400 s, 3000 s and 3600 s, respectively. It can be seen clearly that the growth of junctions exhibited a random patterns and orientations.

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Conflict of interest: The authors declare no conflict of interests.

References

[1] Kim B. H., An J. H., Kang B. A., Hwang K. S., Oh J. S., Nickel-doped titanium oxide films prepared by chemical solution deposition, *J. Ceram. Proc. Res.* **2004** *5* 53–57.

[2] Zaharescu M., Crisan M., Musˇevicˇ I., Atomic force microscopy study of TiO_2 films obtained by the sol-gel method, *J. Sol–Gel Sci. Tech.* 13 **1998** 769–773.

[3] Nishide T., Sato M., Hara H., Crystal structure and optical property of TiO_2 gels and films prepared from Ti-edta complexes as titania precursors, *J. Mater. Sci.* **2000** 35 465–469.

[4] Nakata K. and Fujishima A., TiO_2 photocatalysis: Design and applications**,** *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2012** 13 169– 189.

[5] Fujishima A., Rao T.N. and Tryk D.A., Titanium Dioxide Photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 1, **2000** 1-21.

[6] Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiuchi, Y.; Anpo, M.; Bahnemann, D.W. Understanding TiO_2 photocatalysis: Mechanisms and materials. *Chem. Rev.* **2014**, *114*, 9919–9986.

[7] Suhail M. H., Mohan Rao G. and Mohan S., dc reactive magnetron sputtering of titanium-structural and optical characterization of TiO_2 films, *J. Appl. Phys.* **1992** *71* 1421.

[8] Gyorgy E., Perez del Pino A., Sauthier G., Figueras A., Alsina F. and Pascual J., Structural, morphological and local electric properties of TiO_2 thin films grown by pulsed laser deposition, *J. Phys. D: Appl. Phys.* **2007** 40 5246-5251.

[9] Alzamani M., Shokuhfar A., Eghdam E., Mastali S., Influence of catalyst on structural and morphological properties of TiO_2 nanostructured films prepared by sol–gel on glass. *Progress in Natural Science: Materials International;* **2013** 23(1):77–84.

[10] Qiu, J., Zhang, S., & Zhao, H., Recent applications of TiO_2 nanomaterials in chemical sensing in aqueous media. Sensors and Actuators, *B: Chemical*, **2011** 160(1), 875–890.

[11] Yin, M., Liu, X., Hu, L., Xu, L., & He, J. Effects of Nb doping on microstructure and photocatalytic properties of TiO_2 thin film. Desalination and Water Treatment, **2016** 57(15), 6910–6915.

[12] Azani A., Che Halin D. S., Abdul Razak K., Abdullah M. M. A, Mohd Salleh M. A. A., Mahmed N., Abdul Razak M. F. S., Ramli M. M., Azhari A. W., Chobpattana V, Effect of graphene oxide on microstructure and optical properties of TiO_2 thin film, *IOP Conf. Series: Materials Science and Engineering* 701 **2019** 012011.

[13] Sajid, M. I., Gandhi, V. G., Mishra, M., Tripathi, S., Shripathi, T., Joshi, P. A., & Shah, D. O. Single-Step Synthesis of Silver-Doped Titanium Dioxide: Influence of Silver on Structural, Textural, and Photocatalytic Properties, *Industrial & Engineering Chemistry Research*, **2014** 53, 5749–5758.

[14] Abdul Razak K., Che Halin D. S., Azani A., Abdullah M. M. A, Mohd Salleh M. A. A., Mahmed N., Abdul Razak M. F. S., Ramli M. M., Azhari A. W., Chobpattana V, Microstructural studies of doped PEG Ag/TiO_2 thin film, *IOP Conf. Series: Materials Science and Engineering* 701 **2019** 012004.

[15] Reidy D.J., Holmes J.D., Morris M.A., The critical size mechanism for the anatase to rutile transformation in TiO_2 and doped-TiO_2, *J Eur Ceram Soc* **2006** 26 1527.

 doi:10.20944/preprints202012.0558.v1

[16] Kumar K.P., Keizer K., Buggraaf A.J., Okubo T., Nagamoto H., Textural Evolution and Phase Transformation in Titania Membranes: Part 2, *J Mater Chem* **1993** 3 1151.
[17] Hu L., Yoko T., Kozuka H., Sakka S., Effects of solvent on properties of sol—gel-derived TiO_2 coating films,Thin Solid Films **1992** 219:18.
[18] Kajutvichyanukul P., Ananpattarachai J., Pongpom S., Sol–gel preparation and properties study of TiO_2 thin film for photocatalytic reduction of chromium (VI) in photocatalysis process, *Sci Technol Adv Mater* **2005** 6 352.
[19] Yu B., Leung K. M., Guo Q., Lau W. M. and Yang J., Synthesis of Ag–TiO_2 composite nano thin film for antimicrobial application, *Nanotechnology* **2011** 22 115603**.**
[20] Tian H., Zhang Z. and Liu C., Construction and property of needle-like crystalline AgO ordered structures from Ag-nanoparticles, Electronic Supplementary Material (ESI) for New Journal of Chemistry, **2018**. The Royal Society of Chemistry and the Centre National de la Recherche Scientifique.
[21] Akgun, B.A., Wren, A.W., Durucan, C., Sol–gel derived silver-incorporated titania thin films on glass: bactericidal and photocatalytic activity, *J Sol-Gel Sci Technol* **2011** 58 277–289.
[22] Eckertová L., Mechanism of film formation,*Physics of Thin Films*, **1977**, 72-114.
[23] Lee U.H., Kim M.H., Kwon Y.U., Mesoporous thin films with accessible pores from surfaces. *Bulletin of the Korean Chemical Society***. 2006** 27(6) 808-816.
[24] Vahl A., Veziroglu S., Henkel B., Strunskus T., Polonskyi O., Aktas O. C.,* and Faupel F., Pathways to Tailor Photocatalytic Performance of TiO_2 Thin Films Deposited by Reactive Magnetron Sputtering, *Materials (Basel).* **2019** 12(17) 2840.
[25] Kumar M., Kumar Parashar K., Kumar Tandi S., Kumar T., Agarwal D. C., and Pathak A., Fabrication of Ag:TiO_2 Nanocomposite Thin Films by Sol-Gel Followed by Electron Beam Physical Vapour Deposition Technique, *Journal of Spectroscopy*, **2013**, 491716.