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Synthesis of Ag–TiO_2 Thin Film — Molarity and Temperature Effect on Microstructure

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Ag-TiO_2 thin films with different concentration of silver (Ag) added were successfully deposited onto Si-substrate via sol–gel spin coating method. The phase analysis and microstructures of Ag–TiO_2 thin films have been characterized by X-ray diffractometer and scanning electron microscope. X-ray diffraction spectra show existing different phases influenced by the concentration of the Ag and the annealing temperature. The micrograph of scanning electron microscopy revealed the thin films annealed at 600 °C with 7 mol% of Ag concentration which shows that the Ag particles were found like a white dot formed on the grain of TiO_2 thin films.

topics: Ag/TiO_2 thin film, sol–gel, spin coating, annealing temperature, Ag concentration

1. Introduction

The global economy requires increasingly better materials with unique properties [1–3]. Nowadays, TiO_2 is one of the most popular photocatalysts and widely used in the research due to its high mechanical tensile strength, corrosion stability, and low cost. TiO_2 nanoparticles have been used in many applications due to their outstanding properties. They are used to investigate their properties in the environmental and solar cell application such as the photocatalytic activities and antibacterial activities [4, 5], photovoltaic properties [6], electrooxidation properties [7] and electrochromic application [8].

TiO_2 exists in three main crystallographic forms: anatase, rutile, and brookite. Among them, anatase is previously known as the most photocatalytically active phase [9]. The anatase type may be used in various application, including for disinfecting bacteria. The photocatalytic process will generate hydroxyl radical which can attack the cell walls of bacteria, and can lead to destructing itself [10]. The deposited metals on the surface of TiO_2 can produce traps to capture the photoinduced electrons or holes, leading to the reduction of electron–hole recombination in photocatalytic processes and the increase in the absorption capability for visible light of TiO_2 particles. However, some noble metals such as Pt, Pd, Rh, and Au are too expensive to be used in industrial scale. Ag is the most common additive used to enhance the antibacterial and photovoltaic properties of the TiO_2 thin films [11]. There are various techniques used in thin film preparation such as sol–gel method [7], DC reactive magnetron sputtering [4, 12], RF magnetron sputtering [5], and nebulized spray pyrolysis technique [11]. However, the method used to prepare a thin film may affect its properties. The quality of the deposited films depends on deposition parameters such as withdrawal speed of the dip coating or speed of spin coating, concentration of the precursor solution, and the annealing temperature.

In this paper, the TiO_2 thin films were produced via sol–gel method with different Ag concentration. The effect of molarity and temperature of annealing on the microstructures were investigated. The obtained thin films were characterized using X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX).

2. Methodology

Titanium(IV) isopropoxide (TTIP) was mixed with isopropanol in a ratio of 1:20 (TTIP:isopropanol). The TTIP and isopropanol solution was then stirred by using magnetic stirrer for 1 h in the room temperature and acetic acid was added to the solution during the spinning process until a transparent and homogeneous solution formed. Then, the silver nitrate powder was dissolved in the deionized water to produce $AgNO_3$ solution with concentration of 5 mol.%, 7 mol.%, and no addition of Ag. The different concentration of $AgNO_3$ solution was added by drops into the clear TiO_2 sol solution and continued to stir for another 30 min at room temperature. This modification was focused on concentration of Ag compared to previous studies which was focused on weight of Ag added [13, 14]. The Ag/TiO_2 sol solution was deposited on silicon (Si) wafer by spin coating process. The coated thin film was dried at 60 °C for 10 min before coated the next layer of coating. The obtained thin films were then annealed at 400, 500, and 600 °C for 1 h. The phase composition of the thin film was analyzed by using XRD. The SEM was used to characterize the microstructures.

3. Results and discussion

3.1. Phase determination

Figure 1 shows the XRD spectra of the different concentration of Ag/TiO_2 thin films which was annealed at 400 °C. In the pure TiO_2 thin film as shown in Fig. 1a, no Ag concentration was added. It is clearly seen that the rutile phase of TiO_2 were detected with the peaks labelled (002), (211), and (301). For the thin films with 5 mol.% (Fig. 1b), it can be found that TiO_2 anatase phase with plane of (213) and (122) existed. When the amount of Ag concentration was increased to 7 mol.%, the plane of (122) corresponded to AgO while in the prepared films with 5 mol.%, the plane (122) corresponded to anatase TiO_2 as shown in Fig. 1c.

From the XRD spectra as shown in Fig. 2a, the films were annealed at 500 °C, and it was revealed that only TiO_2 rutile phase had been formed the same as found in Fig. 1a. From Fig. 2b with 5 mol.% of Ag, the anatase phase TiO_2 was found with the phase of AgO while when 7 mol.% Ag concentration added into the parent solution the anatase phase was transformed to rutile phase with the plane of (002) and (301), respectively. A small peak of Ag_2O was formed along with TiO_2 as shown in Fig. 2c.

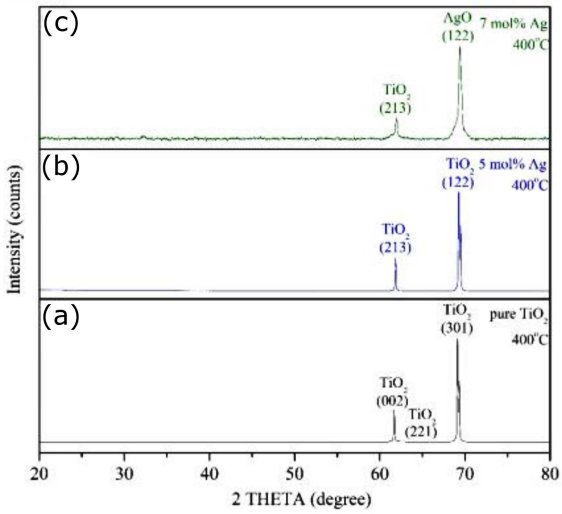

Fig. 1. XRD spectra of films which were annealed at 400 °C for (a) pure TiO_2, (b) 5 mol.% Ag and (c) 7 mol.% Ag.

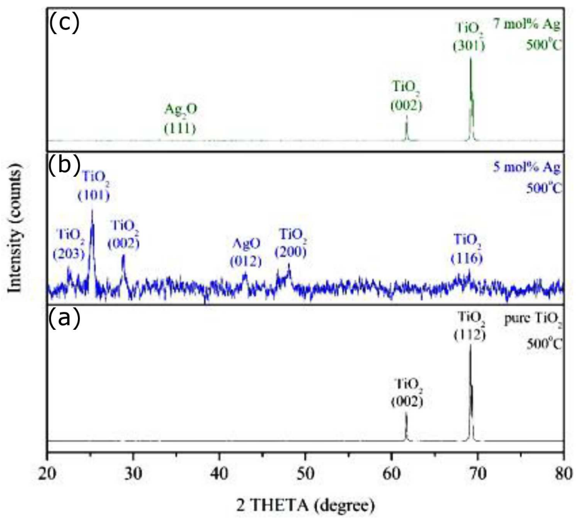

Fig. 2. As in Fig. 1, but for 500 °C.

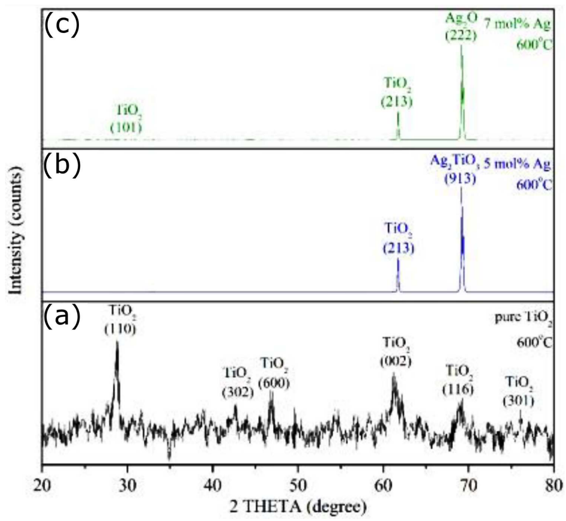

Fig. 3. As in Fig. 1, but for 600 °C.

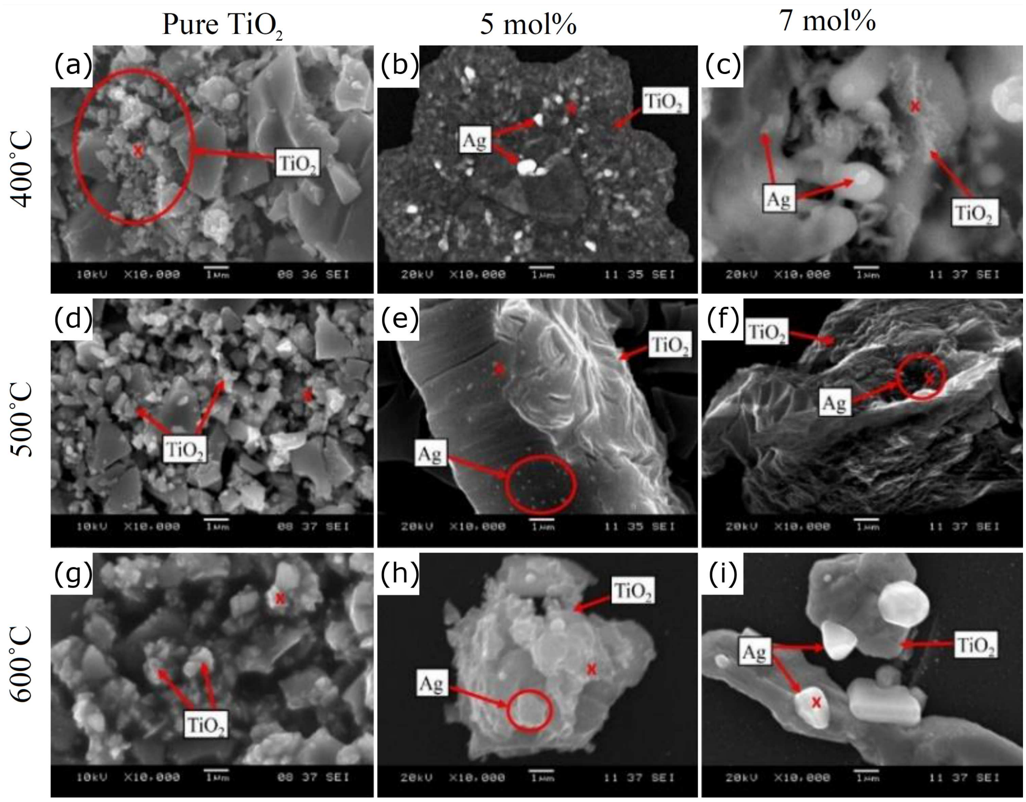

Fig. 4. Micrograph of SEM for the films annealed at 400 °C, 500 °C and 600 °C for pure TiO_2 (labelled as (a), (d), and (g)), 5 mol% Ag (labelled as (b), (e), and (h)) and 7 mol.% Ag (labelled as (c), (f), and (i)).

Figure 3 shows the XRD spectra of thin films annealed at 600 °C. With this annealing temperature, anatase-rutile phase was formed in the pure TiO_2 thin film (Fig. 3a) and 5 mol.% Ag concentration (Fig. 3b). In 5 mol.% Ag concentration, the phase of Ag_2TiO_3 was also formed. With the increase of Ag concentration to 7 mol.%, the anatase-rutile phase was transformed to anatase phase only, while the Ag_2TiO_3 was transformed to Ag_2O phase as shown in Fig. 3c. It is clearly seen that higher Ag concentration results in better crystallinity with stronger lines related to rutile and anatase phase of TiO_2 and metal oxide of AgO, Ag_2O, and Ag_2TiO_3. The spectra of pure TiO_2 film reveal that the film is fully crystallized in rutile phase when the annealing temperature is at 400 °C and 500 °C while at 600 °C the film exists in anatase-rutile phase. It also revealed the annealing temperature of 600 °C with the addition of 7 mol.% of Ag could lead to the formation of metallic oxide of AgO and Ag_2O. It can be concluded that the annealing temperature and Ag concentration are not enough for AgO or Ag_2O to form a pure metallic Ag phase.

3.2. Surface morphology analysis

Figure 4 shows the microstructures of pure TiO_2 films, 5 mol% and 7 mol% of Ag concentration added into the parent solution of TiO_2. All prepared films were annealed at different temperatures: 400, 500, and 600 °C. Figure 4a–c shows the Ag/TiO_2 thin film annealed at 400 °C. From the micrograph, there can be seen that the white spots shown in Fig. 4b and c were Ag particles, which are not present in the pure TiO_2 thin film as seen in Fig. 4a. The effect of Ag concentration on the films annealed at 500 °C was shown in Fig. 4d–f. The white spots with a small dots that were marked in the micrograph corresponded to the Ag particles as shown in Fig. 4e and f. The particles were of irregular shape and had a rough surface. The films which were annealed at at 600 °C were shown in Fig. 4g–i. The micrographs revealed that the grain size of the pure TiO_2 thin film was the biggest as compared to the TiO_2 grain which annealed at 400 °C and 500 °C. A small amount of Ag particles was formed in 5 mol.% Ag concentration as shown in Fig. 4h. Figure 4i shows an irregular shape and size of Ag particles which were grown in the 7 mol.% Ag concentration. It well agrees with the previous work reported, the Ag particles seem brighter than the Ti and O particles because the heavy element backscatter electrons were considered to be stronger than the light element where Ag was the heavy metal and the Ti and O were the light elements [15]. When the annealing temperature increased, the grain size becomes larger. Haider et al. was reported that when the annealing temperature increased, the crystallinity is improved and the crystalline size becomes larger [12].

4. Conclusion

The Ag–TiO_2 thin film was successfully synthesized via sol–gel spin coating method and annealed at different annealing temperatures. The phase analysis and microstructures of the Ag/TiO_2 thin film were characterized by using XRD and SEM. It can be concluded that the results indicate that the silver incorporation and its concentration affect the phase composition and microstructures properties of Ag–TiO_2 thin films. The XRD analysis revealed that the silver is crystallized in metal oxide state such as AgO, Ag_2O, and Ag_2TiO_3.

Acknowledgments

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References

[1] M. Nabiałek, *Archiv. Metall. Mater.* **61**, 439 (2016).

[2] S. Song, H. Shen, Y. Wang, X. Chu, J. Xie, N. Zhou, J. Shen, *Coll. Surf. B Biointerfaces* **185**, 110596 (2020).

[3] K. Jez, M. Nabialek, K. Gruszka, M. Deka, S. Letkiewicz, B. Jez, *Mater. Plast.* **55**, 438 (2018).

[4] G. Kenanakis, D. Vernardou, A. Dalamagkas, N. Katsarakis, *Catal. Today* **240**, 146 (2015).

[5] T. Dhandayuthapani, R. Sivakumar, R. Ilangovan, C. Gopalakrishnan, C. Sanjeeviraja, A. Sivanantharaja, *Electrochim. Acta* **255**, 358 (2017).

[6] P. Pansila, N. Witit-Anun, S. Chaiyakun, *Proced. Eng.* **32**, 862 (2012).

[7] C. Sun, Y. Wang, Q. Su, *Ceram. Int.* **43**, 14537 (2017).

[8] B. Yu, K.M. Leung, Q. Guo, W.M. Lau, J. Yang, *Nanotechnology* **22**, 115603 (2011).

[9] B. Aprianto, Ph.D. Thesis, Universitas Indonesia, Depok 2015.

[10] D.M. Blake, P.C. Mannes, Z. Huang, E.J. Wolfrum, J. Huang, W.A. Jacoby, *Separ. Purif. Methods* **28**, 1 (1999).

[11] L. Lin, H. Wang, H. Luo, P. Xu, *J. Photochem. Photobiol. A Chem.* **307**, 88 (2015).

[12] A.J. Haider, R.H. Al-Anbari, G.R. Kadhim, C.T. Salame, *Energy Proced.* **119**, 332 (2017).

[13] K.A. Razak, D.S.C. Halin, M.M.A.B. Abdullah, M.A.A.M. Salleh, N. Mahmed, N.S. Danial, *Solid State Phenom.* **280**, 26 (2018).

[14] D.S.C. Halin, M.M.A.B. Abdullah, M.A.A.M. Salleh, N. Mahmed, A.N. Mohd Sakeri, K.A. Razak, *Solid State Phenom.* **273**, 140 (2018).

[15] K. Usha, P. Kumbhakar, B. Mondal, *Mater. Sci. Semicond. Process.* **43**, 17 (2016).