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Synthesis of Zn/TiO_2 Thin Films for Self-Cleaning Applications

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Titanium dioxide (TiO_2) thin film has been widely used in semiconductor applications. The surface modification on TiO_2 has been done by adding zinc (Zn) in order to improve surface wettability and enhance the photocatalysis efficiency for solar cell applications. Self-cleaning technology is very important to sustain the efficiency of the solar cell and reduce the cost of the maintenance of the solar cell. In this work, the sol–gel method was used due to the economic factor and its best efficiency. The sol–gel method is a wet chemical technique involving several steps, such as hydrolysis and polycondensation, gelation, aging, drying, densification, and crystallization. The X-Ray diffraction pattern shows that anatase and rutile phases were detected at $2\theta = 36.3864°$. It was clearly seen at 4% Zn-doped TiO_2 annealed at 400°C that due to the increment of Zn concentration, the phase transformed from the anatase phase to the rutile phase at high temperature. The scanning electron microscope micrograph shows that Zn concentration affects grain size. The water contact angle produced when 4% Zn-doped TiO_2 was annealed at 300°C, was 18° — higher than in the sample of 4% Zn-doped TiO_2 annealed at 400°C. These results clearly showed that the dopant concentration and the annealing temperature influence the properties of TiO_2 for a self-cleaning application.

topics: titanium dioxide, self-cleaning, photocatalysis, sol–gel

1. Introduction

TiO_2 is a photocatalyst widely used as a self-cleaning surface due to the capability of TiO_2 of maintaining the surface free of contamination and avoiding dirt deposition. TiO_2 exhibits photocatalytic activity under UV irradiation, which enables the oxidative destruction of a wide range of organic compounds and biological species, causing self-decontamination effect [1–3]. TiO_2 thin films may be deployed on the surface of various substrates and provide layer that exhibits self-cleaning properties when exposed to light. Many studies have been reported on doping with metal oxides to improve efficiency of the TiO_2 photocatalyst [4]. The discovery of the photocatalytic process has become one of the most promising new technologies for the decomposition of different types of pollutants. The photocatalyst can decompose stable organic matter at normal temperature and pressure using sunlight [5]. Well-known types of self-cleaning surfaces are hydrophilic. The hydrophilic coated surface shows a water contact angle $\leq 90°$. Thus, this hydrophilic surface is very suitable for the photocatalysis process in solar cell application as its surface can clean dirt with the water on it instead of droplets [6].

In the previous work, it has been reported that the photocatalytic efficiency can be enhanced by inhibiting the combination of photogenerated electrons and holes [7]. Mei Yang et al. [8] prepared Zn-doped micro-arc oxidation (MAO)-TiO$_2$ films using a titanium substrate and Zn(NO$_3$)$_2$ solution and discovered that Zn doping broadens the absorption spectra and extends the excitation wavelength to the visible light range. In this work, the Zn-doped TiO$_2$ thin films were prepared by the sol–gel method and then annealed at different temperatures. Finally, the effects of Zn concentration and annealing temperature on the phase transformation, microstructure and hydrophilicity properties of TiO$_2$ were discussed.

2. Experimental details

Titanuim isopropoxide (TTIP) was used as a precursor and mixed with ethanol as a solvent. After the mixing process, acetic acid was added to the parent solution as a stabilizer. Also, the dopant of zinc chloride (ZnCl) with different concentrations was added. The volume of every solution was the same but the concentrations were different. Each mixed solution needed to dissolve completely by stirring process at room temperature for 1 h to produce a clear solution. The stirring process had to be vigorous to ensure that each material was uniformly dissolved. The sol solution will then be dropped by pipette onto the glass substrate and deposited by spin coating method. The films were annealed at different annealing temperature and analyzed by X-Ray diffraction (XRD), scanning electron microscope (SEM), wettability test, and UV–Vis spectroscopy.

3. Results and discussion

Figure 1a and b shows the XRD pattern for thin film annealed at 300°C and 400°C, respectively. The peaks obtained by pure TiO$_2$ and 2 wt% of Zn/TiO$_2$ film were not clearly visible. In turn, the peaks obtained for 4 wt% of Zn/TiO$_2$ film annealed at 300°C matched the ICDD card 01-089-4203, showing the existence of anatase phase of TiO$_2$ at $2\theta = 11.5989°$, 32.1069°, 34.7280°, and 36.5845°. At the higher annealing temperature of 400°C with 4 wt% of Zn, the mixed phase of the anatase and rutile phases was exhibited. The Zn ion in TiO$_2$ helps in the rutile phase growth because Zn can interact with the surrounding anatase crystal. Furthermore, the scattering angles will be shifted to smaller angles because the ionic radius of Ti^{4+} is smaller than that of Zn^{2+} [9].

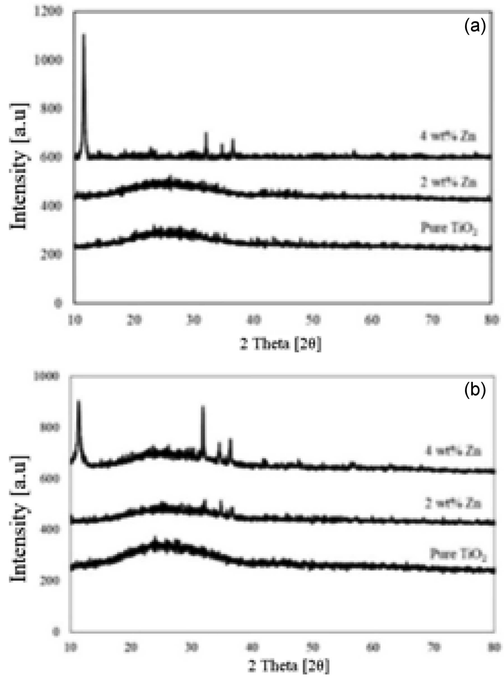

Fig. 1. XRD pattern for pure TiO$_2$ thin film and the Zn/TiO$_2$ thin films with the addition of 2 wt% Zn and 4 wt% Zn that have been annealed at (a) 300°C, (b) 400°C.

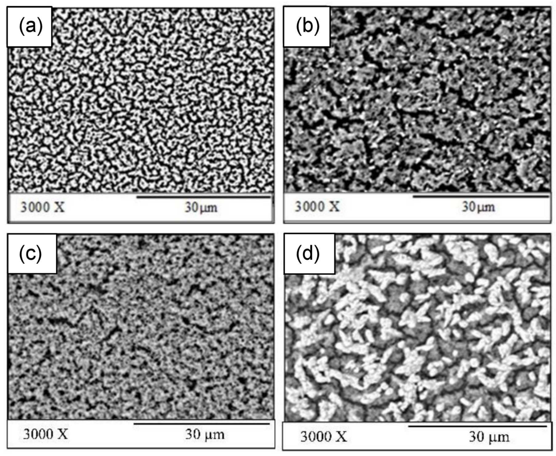

Fig. 2. SEM image for Zn/TiO$_2$ thin films annealed at 300°C and 400°C with the addition of Zn with, respectively, (a, c) 2 wt% and (b, d) 4 wt%.

Figure 2 shows the microstructure image of Zn/TiO$_2$ thin films annealed at 300°C and 400°C. The formation of a small island and the island coalescence with gaps between the other islands is clearly seen for the sample with 2 wt% Zn. The islands start to coalesce and become porous when 4 wt% of Zn is added. In the case of pure TiO$_2$ sample, the nucleation stage is started at an annealing temperature of 400°C, while the formation of the island is scattered, with a huge gap between the other islands. When 2 wt% Zn is added to the TiO$_2$

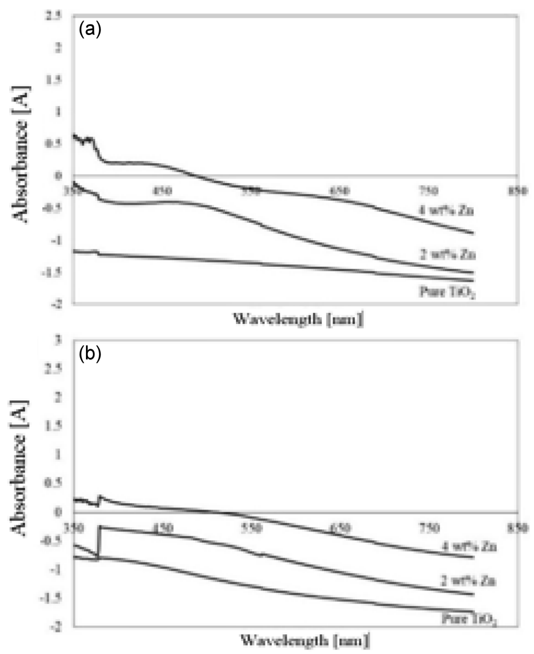

Fig. 3. UV–Vis absorbance spectra of pure TiO_2 and Zn-doped TiO_2 annealed at (a) 300°C and (b) 400°C.

solution, the island start to coalesce and the gap between the islands become small and porous in structure. Note that the structure limits the accessibility of the pore in thin films as the interfacial energy between the substrate's surface and the films often leads to the positioning of the pores parallel to the substrate surface [10].

The water contact angle is in the range of 22–54° for Zn/TiO_2 thin films with 2 wt% Zn and 4 wt% Zn, annealed at 300°C and 400°C, thus they are considered to be hydrophilic surfaces. The films annealed at 300°C and 400°C reveal that the water contact angle decreases to 22° and 40°, respectively, when doped with 4 wt% of Zn. Previous results on water contact angle on the pure TiO_2 surface are contradictory and ranging from 72° by Wang et al. [11] to 33.3° by Sakai et al. [12] and 15° by Watanabe et al. [13], depending on the film structure and storage conditions. This clearly indicates that the films with 4 wt% Zn and low annealing temperature are significantly different from the pure TiO_2 films and show super-hydrophilicity with a water contact angle near 0°. However, further increasing the Zn content up to 4% had no further drastic effect on the water contact angle on the coatings.

The optical absorbance spectra of pure TiO_2 and Zn-doped TiO_2 annealed at 300°C and 400°C were shown in Fig. 3a and b, respectively. The absorption spectra show the shift of the light absorption edge of the Zn-doped TiO_2 films as compared to the pure TiO_2 film. The band gap energy can be estimated from the value of the wavelength, at which the absorption edge starts to take off, and the value of the band gap energy of the TiO_2 films with the addition of different wt% of Zn. It can be observed that the band gap energy decreases marginally for the films annealed at 300°C, from 3.83 to 3.10 eV, and for the films annealed at 400°C, it decreases from 3.38 to 3.18 eV. The shift has been attributed to the formation of impurity by the dopant within the band gap states of TiO_2 [14].

4. Conclusions

In this work, pure TiO_2 and different amount [wt%] of Zn added using the sol–gel spin coating method were prepared. It was found that 4 wt% of Zn/TiO_2, when annealed at 300°C, form anatase phase, and a mixed phase of anatase and rutile, when annealed at 400°C. The microstructure revealed that the coalescences of the porous-like structures for the TiO_2 thin film occur at 300°C and become denser at 400°C. The observed wettability test shows the hydrophilic surface of the films. Finally, the absorption spectra show the shift of the light absorption edge of the Zn-doped TiO_2 films as compared to the pure TiO_2 film, and the band gap decreases from 3.83 to 3.10 eV at 300°C and from 3.38 to 3.18 eV at 400°C. Therefore, the addition of Zn and annealing temperature will have an effect on the properties of the obtained Zn/TiO_2 thin films, making them suitable for use as a self-cleaning material.

Acknowledgments

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