Microstructural studies of doped PEG Ag/TiO$_2$ thin film

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Abstract. Ag/TiO$_2$ thin film was prepared by the sol-gel method through the hydrolysis of titanium tetraisopropoxide and silver nitrate solution. Various amount of PEG was doped into the solution preparation to study the effect on crystalline state and microstructural of the prepared thin films. Spin coating method was used to get uniform film on ITO glass substrate followed by annealing process for 1 hour. The obtained thin films were analysed using XRD test, SEM and AFM. Results showed that all the prepared thin films are in anatase TiO$_2$. Increasing the PEG amount into the solution could increase the thickness and surface roughness of the obtained thin films.

1 Introduction

Titanium dioxide known as titanium (IV) dioxide or titania has a molecular weight of 79.87 g/mol which is a natural titanium oxide with TiO$_2$ chemical formula. Titanium dioxide is a substance commonly used as white pigment due to its remarkable properties such as high purity, brightness, and non-toxicity. It is also known for its excellent chemical stability, biologically non-toxic and low cost [1]. It is an important inorganic functional material with good physical properties, making it ideal for thin film applications. TiO$_2$ thin films are one of the most important oxides due to their attractive chemical, electrical and optical properties [2-4]. TiO$_2$ has been studied by many researchers because of its many applications in various industries [5-7]. Due to its high corrosion resistance and chemical
stability, excellent optical transparency near infrared and visible areas, it provides a high refractive index which makes it useful for anti-reflection coating in optical devices [8].

Additives are used to enhance the performance and simultaneously improve the coating of the thin film. Additives can be in many types of materials or chemicals. The additive was found to improve the surface area whereby increase the surface area resulting the great efficiency of prepared thin films. Polyethylene glycol (PEG) is made up of various sizes and functional groups that are synthetic polymers [9]. These attractive additives are also known as polymer additives which have several advantages over the resulting coating such as adding active surface area with porous surface structure due to pore formation and reducing energy gap in TiO₂ [10]. Porous films have been obtained by using PEG as a chelating agent [11]. In this research, we focused on the effect of the addition of PEG into Ag/TiO₂ thin films.

2 Materials and Preparation of Ag/TiO₂ Thin Films

Titanium (IV) isopropoxide 97% (TTIP) and silver nitrate (AgNO₃) powder were obtained from Sigma Aldrich. Propan-2-ol was purchased from QReC Chemicals and acetic acid (99.5%) and methylene blue were obtained from Daejung Reagent Chemicals and respectively. All the chemicals were analytical reagents and were used as received without further purification.

The Ag/TiO₂ thin film without PEG was prepared as in previous study [12]. Then, for the Ag/TiO₂ thin film with PEG, a different amount of PEG (0.05g, 0.10g, 0.15g and 0.20g) was added into the solution after the 25 min sol stirring. The resultant alkoxide solution was kept stirring at room temperature until a clear sol produced, without any precipitation. ITO coated glass (15mm×15mm×0.5mm) were used as the substrates for the deposition of films.

The prepared Ag/TiO₂ thin films were characterised structurally through XRD and morphologically by SEM. The phase composition of the synthesized thin film were determined by using an X-ray diffraction (XRD) over a 2θ range 10°- 65° using Cu Kα (λ=1.5046). Analysis of the XRD patterns was carried out using Diffrac Eva Software. Surface morphology and surface roughness of prepared the thin films were observed via SEM and AFM.

3 Results and Discussions

3.1 Phase and Crystallite Size Analysis

X-ray diffraction analysis of Ag/TiO₂ thin films with different amount of PEG deposited on ITO substrate is shown in Fig. 1. All the films present five strong diffraction peaks located at 21.51°, 30.57°, 35.40°, 51.04° and 60.70°. These peaks are attributed to the ITO substrates, SiO₂ and In₂O₃ peaks. As can be seen, a small peaks at 25.30° which are assigned to TiO₂ anatase (101) plane, referring to JCPDS JCPDS PDF-021-1272. No diffraction peak of silver is detected which can be explained by the dominance of the ITO peaks in the spectrum with their high intensities, making it difficult to detect silver existing in low amounts [13]. A small peak located at 33.66° is assigned to silver oxides, Ag₂O (100) plane, according to JCPDS No 01-072-2108. However, the X-ray diffraction pattern for the doped PEG Ag/TiO₂ thin film showed the intensity of the diffraction lines is gradually decrease
with the increasing amount of PEG. The addition of the PEG 2000 in the Ag/TiO$_2$ influenced on the unit cell parameters of anatase [14]. The intensity of the diffraction peak decreases and the amplitude of the diffraction peak decreases, indicating that TiO$_2$ crystalline size is decreasing, consistent with studies conducted by previous researchers [15-17].

![XRD pattern of Ag/TiO$_2$ thin films with different amounts of polyethylene glycol](image.jpg)

Fig. 1: XRD pattern of Ag/TiO$_2$ thin films with different amounts of polyethylene glycol

As can be seen, the intensity of the diffraction peak decreases and the apex aperture decreases, indicating that TiO$_2$ crystalline size decreases, consistent with a study conducted by previous researchers [15-17]. The graph in Fig. 2 shows the crystalline size distribution of Ag/TiO$_2$ thin films produced with different PEG amounts. The crystalline size is calculated from the Debye-Scherer formula using the XRD extension. Overall, the TiO$_2$ crystalline size decreased with the addition of PEG additives. According to [16], the presence of PEG in the Ag/TiO$_2$ thin film layer reduced the size of the crystals, but did not reduce the amount of TiO$_2$ anatase crystals that were an important factor in the photocatalytic process. The Ag/TiO$_2$ thin film crystals were reduced from 40.39 nm to 29.78 nm, 23.88 nm, 19.62 nm and 23.63 nm with the addition of PEG weights of 0.05 g, 0.10 g, 0.15 g and 0.20 g, respectively. The smallest crystals recorded were 0.15 g of PEG, 19.62 nm, which is approximately 105% of the Ag/TiO$_2$ thin film structure that was not added to PEG, 40.39 nm.
According to Petrik et al. [18] during the Ag/TiO$_2$ thin film synthesis process, the PEG molecules are absorbed externally into the -Ti-O-Ti- oligomers and form a hydrogen bond. The subsequent formation and polymerization process consists of the formation of an oligomer/PEG composite, in which PEG determines the size of the crystals formed.

3.2 Morphological Observations

The surface morphology of Ag/TiO$_2$ thin films with different amounts of PEG was observed under SEM as shown in Fig. 3. All the prepared Ag/TiO$_2$ thin films are uniform and evenly distributed in uneven shape and porous structure. From Fig. 3(b), Ag/TiO$_2$ thin film with the addition of 0.05g of PEG shows a thin film with a series of a small, coarse and loose crystalline structures compared to the non-PEG thin film structure (Fig. 3(a)), with a larger and thicker structure, in line with the crystalline size obtained from XRD analysis. The PEG 2000 additives in the Ag/TiO$_2$ solvents act as a dispersion agents, where the low TiO$_2$ particle aggregation can be explained by the presence of a steric barrier. PEG additives ensure that the soluble particles are separated in solution due to the dispersion of polymers as long-chain molecules [17]. However, no significant changes were observed in the surface morphology of the Ag/TiO$_2$ thin films when the amount of PEG was increased from 0.10g to 0.15 and 0.20g as shown in Fig. 3 (c) to Fig. 3 (e). Structural changes on the surface of the resulting thin films were due to the thermal decomposition of PEG during the annealing process which led to the formation of coarse and porous structures. A similar situation has been reported by previous researchers [13].
In order to investigate the effect of PEG addition on the morphology and surface roughness of the resulting Ag/TiO₂ thin films, AFM analysis was performed. Fig. 4 shows the topography and 3D views of the surface structure of the thin films produced, while Table 1 shows the surface roughness of Ag/TiO₂ thin films with different PEG amounts. It can be clearly seen that the structure of the Ag/TiO₂ thin film without the addition of PEG is smooth, uniform and covers the entire surface of the substrate, Fig. 4 (a). The maximum height of this film was 14.98nm with an average roughness of 1.81nm. When 0.05g of PEG was added, the resulting film structure changed to a coarse, non-uniform form, as shown in Fig. 4 (b). The maximum height of this film was 36.29nm with the average roughness slightly increase to 5.88nm.

Furthermore, when the added PEG weight is increased to 0.10g, 0.15g and 0.20g, the resulting Ag/TiO₂ thin film structures becomes rough and porous. The Ag/TiO₂ films thickness were also increased with the maximum layer thickness recorded at 229.67 nm, 279.49 nm and 300.80 nm. The root mean square roughness of the film also increased with increasing PEG weight to 39.5nm, 44.71nm and 49.37nm. The differences in the surface morphology of the resulting films can be explained by the formation of pores within the Ag/TiO₂ film layer due to PEG thermal decomposition during the annealing process [13]. When more amount of PEG added to the sol solution, the viscosity of the sol increased. The solution attached to the substrate increase and make the resulting thin film layer thicker. Tiwari et al., [19] in their study also found that the TiO₂ thin film coated with PEG was thicker than the non-PEG coated film.
Fig. 4: Surface morphology of Ag/TiO₂ thin films with different amounts of polyethylene glycol
Table 1: Surface roughness of Ag/TO\textsubscript{2} thin film with different amount of polyethylene glycol

| Ag/TO\textsubscript{2} thin film | PEG weight (g) | Surface roughness, Ra (nm) | Surface roughness, RMS (nm) |
|---------------------------------|----------------|-----------------------------|-----------------------------|
| (a)                             | 0.00           | 1.38                        | 1.81                        |
| (b)                             | 0.05           | 3.60                        | 5.88                        |
| (c)                             | 0.10           | 30.71                       | 39.5                        |
| (d)                             | 0.15           | 35.55                       | 44.71                       |
| (e)                             | 0.20           | 38.78                       | 49.37                       |

4 Conclusion
This work observes the effect of various PEG amounts on morphological and optical properties of Ag/TO\textsubscript{2} thin films. The XRD pattern showed the presence of anatase TiO\textsubscript{2} and Ag\textsubscript{2}O phases. The Ag/TO\textsubscript{2} thin films shows a rough and porous surface morphology. The surface roughness of the film increased with the increasing of PEG amounts.

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