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Microstructural Study on Ag/TiO₂ Thin Film

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The synthesis of Ag/TiO₂ thin film was carried out by the sol-gel spin coating method using ITO glass as a substrate in a short period of stirring time, which is less than 25 min. The produced films were annealed in a furnace at 500°C for 1 h. Various concentrations of AgNO₃, from 0.1 to 0.9 M, were added. The as-prepared films were characterized using X-ray diffraction, scanning electron microscopy, and atomic force microscopy. The results indicate that all films showed a single phase of anatase, TiO₂. Ag/TiO₂ thin films with 0.1 M of AgNO₃ solution show that the elements form networks connecting Ag/TiO₂ microstructures forming a porous, consistent, and continuous layer on the substrate surface.

topics: Ag/TiO₂ thin film, Ag concentration, microstructural, sol-gel spin coating

1. Introduction

Titanium dioxide (TiO₂) is a material often used as white pigment, being one of the most outstanding, well-known materials because of its superb properties like non-toxicity, high purity, and brightness. It is also known to be economical and has good chemical stability [1]. TiO₂ is an essential inorganic functional substance with good physical properties, making it perfect for thin film applications [2–5]. Many researchers have been studying its applications in various industries and its self-cleaning ability [6–9].

The additives are used to improve performance and, at the same time, improve the coating. Various types of substances or chemicals can be used as additives. We know from the previous research [10], that there are many parameters that influence the film's performance as one of the factors.

In this project, TiO₂ thin films were produced with different concentrations of Ag. The effects of different molarity of Ag on the microstructures were explored. The obtained thin films were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental details

Titanium (IV) isopropoxide (TTIP) was stirred with isopropanol in a ratio of 1:20 (TTIP:isopropanol). The TTIP and isopropanol solution was continued to be stirred using a magnetic stirrer for 10 min at room temperature, followed by a mixture of various concentrations of AgNO₃ (0.1, 0.3, 0.5, 0.7 and 0.9 M), ethanol, and water. Acetic acid was added to the solution as a catalyst until a transparent and homogeneous solution was formed. This modification focuses on

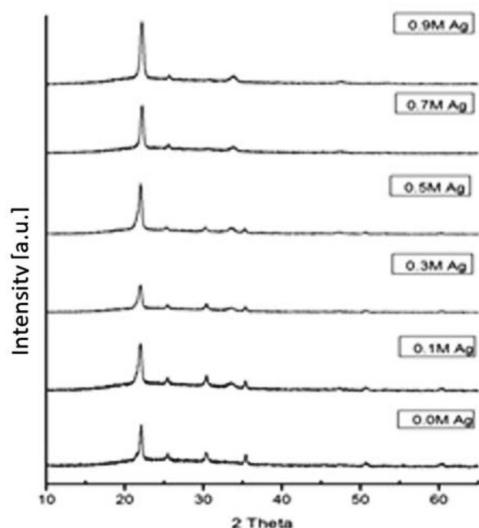


Fig. 1. XRD diffraction of Ag/TiO₂ thin film with various concentrations of AgNO₃.

the concentration of Ag, in contrast to previous studies, which focused on the weight of Ag added. The Ag/TiO₂ sol solution was coated on ITO glass by a spin-coating process. The coated thin film was put to dry at 60°C for 10 min before being coated with the next layer of coating. The obtained thin films were then annealed for 1 h at microstructures and the atomic force microscopy (AFM) was used to analyze the topography and roughness of their surface.

3. Results and discussion

3.1. Phase determination

X-ray diffraction (XRD) analysis was performed on TiO₂ and Ag/TiO₂ thin films with the addition of five different concentrations of silver nitrate (AgNO₃) solutions of 0.1, 0.3, 0.5, 0.7, and 0.9 M. Figure 1 presents the XRD spectra for all thin films. The highest emission peak at $2\theta = 21.51^\circ$ corresponds to the presence of the SiO₂ element and is followed by an angle of $2\theta = 30.58, 35.46, 51.03,$ and 60.70° corresponding to the peak of the indium tin oxide glass coated substrate with JCPDS PDF card 01-088-2160.600°C.

The resulting emission peaks indicate that the peak values of $2\theta = 25.31^\circ$ correspond to the typical structure of TiO₂ tetragonal anatase with planes (101) referring to the JCPDS card PDF 01-078-2486. Previous researchers [11] assert in their report that the peak at $2\theta = 25.31^\circ$ must refer to the structure of the TiO₂ anatase. The addition of AgNO₃ solution did not affect the crystallization of TiO₂ [12].

Out of all the different concentrations in Ag/TiO₂ thin films studied, no peak was identified to indicate the presence of Ag elements. This indicates that it

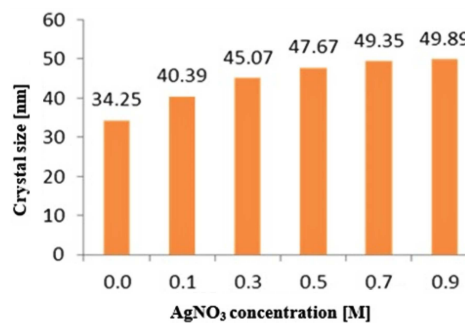


Fig. 2. Crystallite size of Ag/TiO₂ thin film with various concentrations of AgNO₃.

is highly probable that the Ag metal element is well dispersed on the TiO₂ surface in the form of nano-clusters, and, consequently, it cannot be detected by X-ray emission due to little quantity of Ag [13]. Previous researchers [14] have reported that the added metal element lies only on the surface of TiO₂ crystals without being covalently bonded to the crystalline lattice. Therefore, this metal element is below the visible limit of X-ray analysis. The additives may enter the TiO₂ atomic lattice by immersion or as a replacement fluid. The properties of crystalline structures such as electronegativity, valence bands, and atomic size will determine the substitution if they correspond to the TiO₂ lattice. In this case, the Ag⁺ ion radius is 0.115 nm, which is larger than the TiO₂ radius, i.e., 0.0605 nm. Thus, it is quite difficult for Ag⁺ ions to intervene between TiO₂ ions, and they will only exist on the surface of the TiO₂ layer [15].

Based on the XRD results, it is possible to observe the existence of a peak at an angle of $2\theta = 33.66^\circ$, which corresponds to the Ag oxide peak Ag₂O (JCPDS No 01-072-2108) with the (100) plane. The peak intensity of silver oxide, Ag₂O, increased with the increasing concentration of AgNO₃ solution. The excitation peak intensity of indium oxide, In₂O₃, on the substrate decreased and subsequently disappeared with increasing concentration of AgNO₃ solution. This may be due to the presence of large amounts of Ag₂O particles covering the whole surface of the substrate, causing the In₂O₃ to decrease. The peak of TiO₂ anatase decreases and gradually narrows, indicating the increase in crystallite size of TiO₂.

Figure 2 presents the crystallite size of the Ag/TiO₂ thin films with the addition of different AgNO₃ solution concentrations. The Debye–Scherrer formula using XRD extensions was used to calculate the particle size.

3.2. Surface morphology analysis

Figure 3 shows the image of surface morphology of Ag/TiO₂ thin films with different AgNO₃ concentrations labeled with (a) 0, (b) 0.1, (c) 0.3, (d) 0.5,

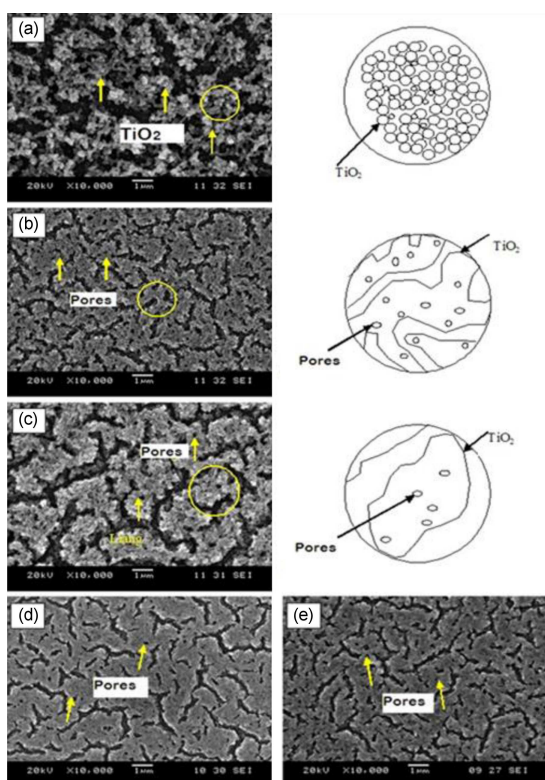


Fig. 3. SEM Micrograph of the Ag/TiO₂ thin films with different concentrations of AgNO₃: (a) 0, (b) 0.1, (c) 0.3, (d) 0.5, (e) 0.7 and (f) 0.9 M.

(e) 0.7 and (f) 0.9 M. The concentration of the precursor used will influence the growth of TiO₂ particles, meaning that the ratio between the precursor and solvent used, the additives used, the catalyst, the preparation method, and the annealing temperature applied will influence the growth of TiO₂ particles. In this study, the ratio of precursor material (TTIP), solvent (isopropanol), and acid (acetic acid) used was 1:40:1.

Referring to Fig. 3a, it can be observed that the TiO₂ thin film microstructure consists of spherical elements, and it is uniformly dispersed on the surface of the substrate. We know from XRD analysis that the TiO₂ element is in the anatase phase, and the same shape has been reported by previous researchers [16]. When 0.1 M of AgNO₃ solution was added to TiO₂ solution, significant changes were observed in the surface morphology of the thin films. This has resulted in the elements forming networks of connections. The thin film of Ag/TiO₂ structures is presented in Fig. 3b. The presence of AgNO₃ in the thin film forms a linker that unites the TiO₂ particles and forms a connecting structure. The addition of a further concentrated AgNO₃ solution has shown that the thin film structures couple with the heavier AgNO₃ solution, which is 0.5, 0.7, and 0.9 M. The addition of more concentrated AgNO₃, which is 0.3 M, has led to a bigger and more compact thin film structure, as shown in Fig. 3c.

The same microstructures can be observed for the Ag/TiO₂ with more concentrated AgNO₃. It is compact, and the structures look like muddy soils and spread evenly across the surfaces of the substrate, as appears in Fig. 3d–f. This proves that as the concentration of AgNO₃ increases, the crystallite size also increases, as shown in Fig. 2.

4. Conclusions

The Ag/TiO₂ thin film was successfully synthesized by using the sol-gel spin coating method with different concentrations of AgNO₃ solutions. Through the XRD analysis, it can be concluded that the silver is crystallized in a metal oxide state as Ag₂O, and the addition of silver (Ag) to the TiO₂ thin film has resulted in the silver incorporation, where its concentration does not affect the phase. However, the addition of AgNO₃ increases the crystallite size of TiO₂ according to the increment of its concentration.

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