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Microstructural Studies of Ag/TiO_2 Thin Film; Effect of Annealing Temperature

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Abstract

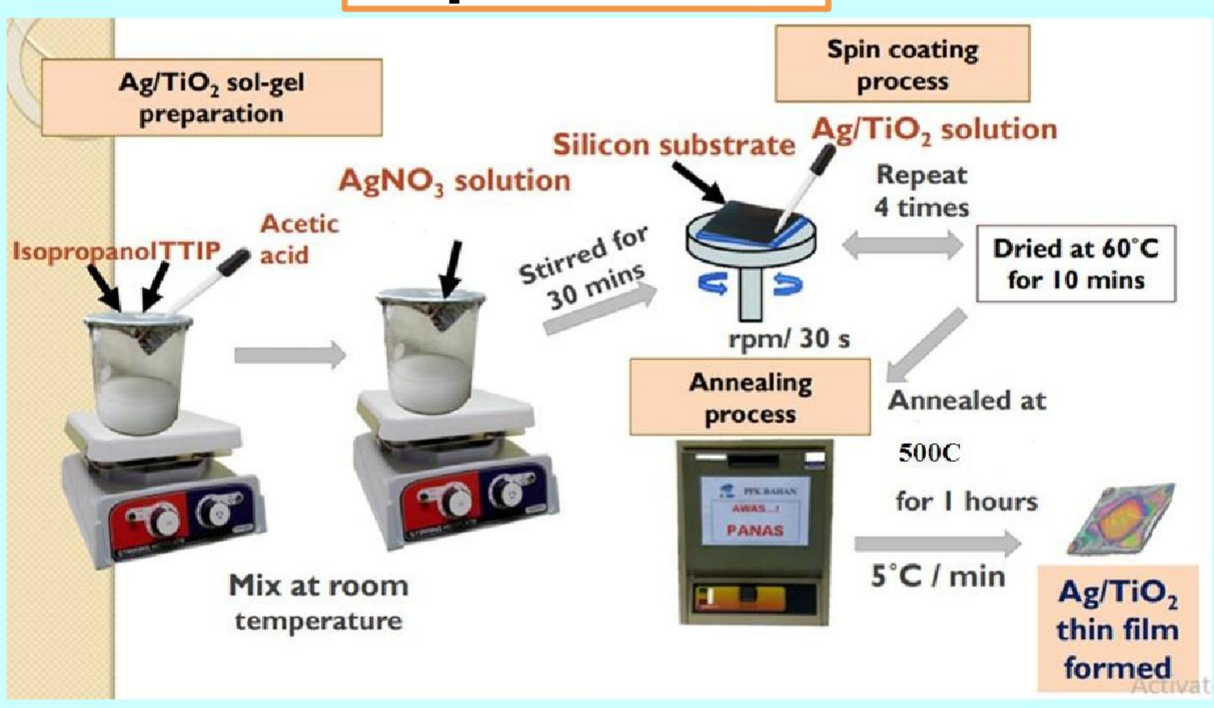
Microstructures are an important link between materials processing and performance, and microstructure control is essential for any materials processing route where the microstructure plays a major role in determining the properties. In this work, silver-doped titanium dioxide (Ag/TiO_2) thin film was prepared by the sol-gel method through the hydrolysis of titanium tetra-isopropoxide and silver nitrate solution. The sol was spin coated on ITO glass substrate to get uniform film followed by annealing process for 2 hours. The obtained films were annealed at different annealing temperatures in the range of 300 °C - 600 °C in order to observe the effect on crystalline state, microstructures and optical properties of Ag/TiO_2 thin film. The thin films were characterized by X-Ray diffraction (XRD), scanning electron microscopy (SEM), and UV-Vis spectrophotometry. It is clearly seen, when the annealing temperature increases to 500 °C, a peak at 2θ = 25.30˚ can be seen which refers to the structure of TiO_2 tetragonal anatase. The structure of Ag/TiO_2 thin film become denser, linked together, porous and uniformly distributed on the surface and displays the highest cut-off wavelength value which is 396 nm with the lowest band gap value, which is 3.10 eV.

Introduction

Many studies on synthesis of TiO_2 and its thin films formed via conventional and advanced sol-gel methods have been reported. Previous investigations show that the properties of TiO_2 films appear to strongly effect on the process parameters and precursors used in the processes. Therefore, most of researchers have used sol-gel method to synthesis TiO_2 thin films with different controlling parameters such as temperature and time of annealing, number of dipping or spinning, molar ratio of prepared solution, precursor solutions and the surfactant or dopant which were used in their research in order to get pure TiO_2 or to enhance the properties of TiO_2 for a certain application. Microstructures are an important link between materials processing and performance, and microstructure control is essential for any materials processing route where the microstructure plays a major role in determining the properties. In the application of photocatalysis devices, the synthesized microstructure strongly affected the performance of harvesting the sunlight.

In this study, Ag/TiO_2 thin films were prepared via sol-gel spin-coating method using a specific ratio. The obtained thin films were annealed in various temperature to investigate the effect of annealing temperature on the crystalline state, microstructures and optical properties of Ag/TiO_2 thin film.

Experimental



Results and Discussion

Fig.1. XRD patterns of Ag/TiO_2 thin films with different annealing temperatures

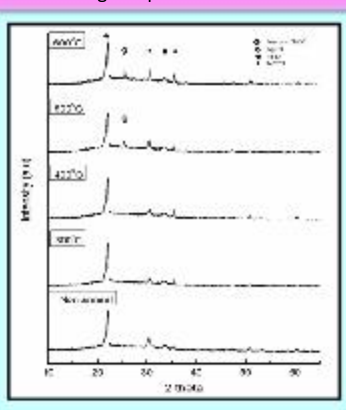


Fig.4. Absorption curve of Ag/TiO2 thin film at different annealing temperature in the spectrum range of 300nm to 500nm

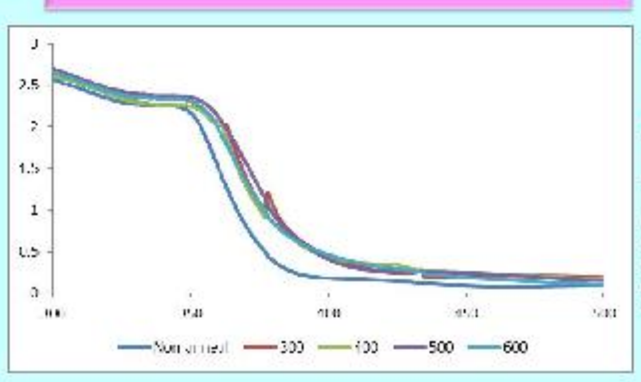


Table 2. Band gap value for Ag/TiO_2 thin film with different annealing temperature

Annealing temperature (°C)	Cut-off wavelength (nm)	Band gap (eV)
Non-annealed	379	3.27
300	382	3.45
400	388	3.19
500	396	3.10
600	390	3.18

Fig. 1 shows the XRD patterns of Ag/TiO_2 thin film at different annealing temperature. There are five peaks at 2θ = 21.5°, 30.57°, 35.40°, 51.04° and 60.70° corresponding to the peaks of ITO glass substrate. No trace of TiO_2 peaks can be observed for the non-annealing film and the films that were annealed at 300 °C and 400 °C, respectively, which might indicates that TiO_2 is still in an amorphous phase. In this case, the thermal energy supplied by those annealing temperature range is not sufficient for the crystallization process to occur [9]. When the annealing temperature were increased up to 500°C, it can be clearly seen a (101) anatase peak at 2θ = 25.30˚ (JCPDS PDF-021-1272). The intensity of this peak becomes stronger as the annealing temperature was increased to 600°C.

Fig. 4 shows the light absorption of Ag/TiO_2 thin film at different annealing temperature in the spectrum range of 300 nm to 500 nm. The absorption edge shifts as the annealing temperature increase. Non-annealed Ag/TiO_2 thin film exhibits low absorption which is 0.57 (arbitrary unit) at wavelength 375 nm and increase to 1.07 (arbitrary unit) when annealed at temperature of 300 °C. Ag/TiO_2 thin film with 500 °C annealing temperature shows the highest absorption at 375 nm wavelength which is 1.17 (arbitrary unit). Value of cut-off wavelength increase as the annealing temperature increase.

Table 2 present cut-off wavelength value and band gap value for Ag/TiO_2 thin film annealed at different temperature. Overall, the cut-off wavelength for all produced thin films are in the spectrum range exceeded 369 nm, which are higher than anatase TiO_2 cut-off wavelength values [15].

Results and Discussion

Fig.2. SEM micrograph of Ag/TiO_2 thin film with different annealing temperature, (a) non-annealing, (b) 300 °C, (c) 400 °C, (d) 500 °C and (e) 600°C

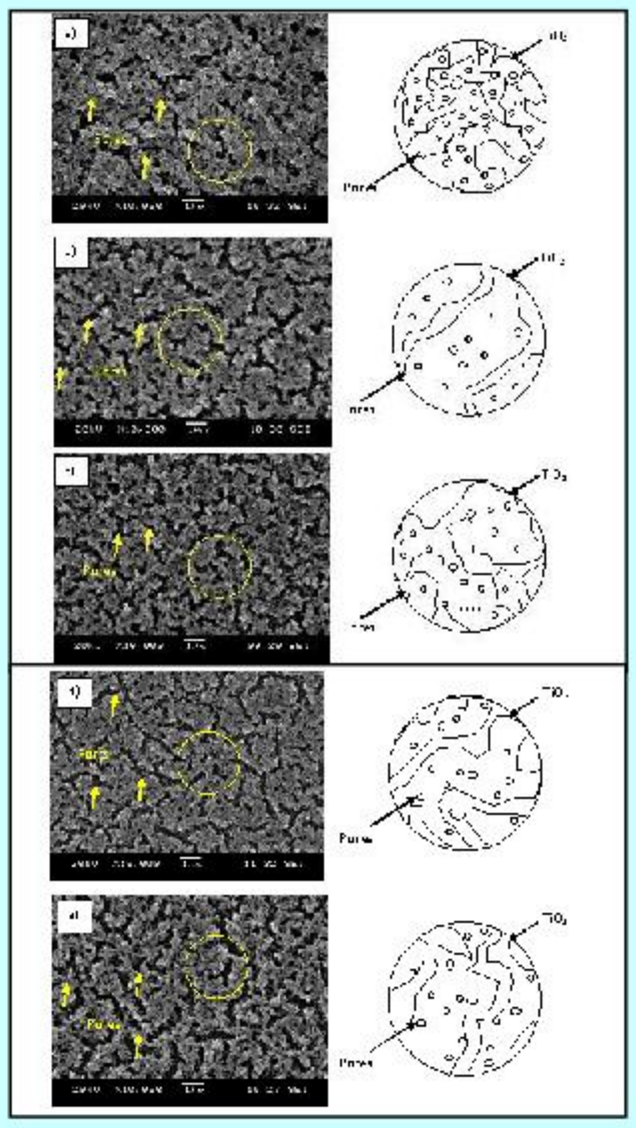


Fig.3. Surface morphology of Ag/TiO_2 thin films at different annealing temperature, (a) non-annealing, (b) 300 °C, (c) 400 °C, (d) 500 °C and (e) 600°C

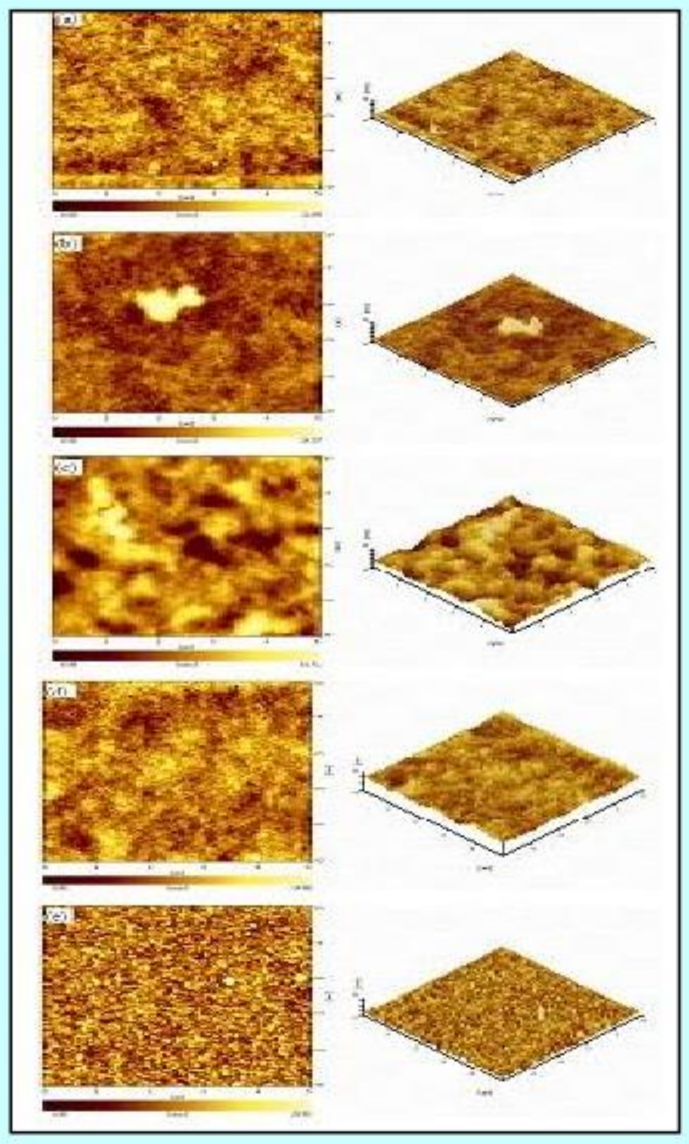


Fig. 2 shows the SEM images of obtained thin films with non-annealing and various annealing temperature. For the non-annealed film [Fig. 2(a)], the film structure was porous and uniformly distributed throughout the substrate, with non-homogenous shapes. As the thin films were annealed at 300 ˚ C and 400 ˚ C, a chain-like structure could be detected, that linked the structures together, as shown in Fig. 2(b) and Fig. 2(c). During the heat treatment up to 200 ˚ C, most organic solvents were burned, leading to the formation of the porous and amorphous structure of the TiO_2 film [12]. When the thin film was annealed at 500 ˚ C, the structure become denser, linked together, porous and uniformly distributed on the surface as shown in Fig. 2 (d). At this stage, the TiO_2 sol had enough energy to crystallize into the anatase phase as proved by the XRD pattern in Fig.1. When the annealing was increased to 600 ˚ C, as seen in Fig. 2(e), the thin film was in porous structure with a wider distance between the linkage of the TiO_2.

As observed in Fig. 3 (a), non-annealed thin film exhibits a rough structure uniformly distributed throughout the substrate, but the crystal grain cannot be seen clearly. This indicates that the thin film particle is in an amorphous phase with surface roughness of 1.81 nm. According to Mosquera et al. (2015), rough stucture and the absence of a fine atomic terrace indicates that the sample deposited as amorphous [14]. After annealing process at 300 °C, the obtained thin film structure is not much different from the non-annealed thin film but the surface roughness increases to 4.36 nm, as shown in Fig. 3 (b). There is also agglomeration of particles which display a non-uniform particle distribution. At 400˚ C annealing temperature [Fig. 3 (c)], the Ag/TiO_2 thin film shows a rough and porous structure. For a thin film that heated over 200 °C, most of the organic solvent were decomposed, thus forming a porous and amorphous TiO_2 thin film [12]. Increasing of annealing temperature can cause the grain to agglomerate thus makes the surface rugged with surface roughness of 9.68 nm. This uneven shape of nanoparticles was caused by low temperature and not enough kinetic energy to induce the crystallization of the particles [9].
At 500°C annealing temperature, the thin film shows a fine structure with small grain size, as seen in Figure 3 (d). At this state, TiO_2 particles have enough energy to crystallize into anatase phase, as proved by the XRD analysis. When the annealing temperature was increased to 600 °C, the grain structure of the thin film became bigger that resulting in a rough surface with surface roughness of 3.92 nm. Increasing the annealing temperature could increase the grain size of the TiO_2 particles and resulting on the increasing of surface roughness due to microstructure phase transformation [14].

Conclusion

(a) The XRD pattern clearly shows the anatase phase when the annealing temperature increased to 500 °C and 600 °C.
(b) The SEM micrograph showed that for the non-annealing film, the film structure was porous and uniformly distributed throughout the substrate, with non-homogenous shapes. When the thin film was annealed at 500 ˚ C, the structure become denser, linked together, porous and uniformly distributed on the surface
(c) Surface topographical profile shows that non-anneal thin film exhibits a rough structure uniformly distributed throughout the substrate, but the crystal grain cannot be seen clearly. This shows that this thin film particle is in amorphous phase with surface roughness of 1.81. At 500 C annealing temperature, the thin film shows a fine structure with small grain size. At this state, TiO_2 particles had enough energy to crystallize into anatase phase, as proved by the XRD analysis. When the annealing temperature increases to 600 C, the grain structure of the thin film becomes bigger and resulting in a rough surface with surface roughness of 3.92.
(d) The light absorption edge shifts as the annealing temperature increase. Ag/TiO_2 thin film that have been annealed at 500 °C displays the highest cut-off wavelength value which is 396 nm with the lowest band gap value, which is 3.13 eV.

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