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Microstructure and phase structure of titanium dioxide films prepared by screen-printing technique

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ABSTRACT This paper deals with the characterization of titanium dioxide, TiO_2 film, which was deposited on ITO covered-glass substrate by screen-printing technique. The films were deposited once and twice on the substrate and then annealed at temperature of 300°C, 350°C and 400°C. The films were characterized by the techniques of x-ray diffraction (XRD), energy dispersive analysis by x-rays (EDX) and scanning electron microscopy (SEM). The results are presented in this paper.

(Screen-printing technique, Titanium dioxide, SEM, XRD)

INTRODUCTION

The fabrication of the thin film material on the substrate can be employed by various techniques, namely, electron sputtering, electron beam evaporation, spraying pyrolysis and screen-printing. Screen-printing in fabricating film material is a relatively cheap and simple technique as compared to the other techniques, since the same equipment can be used for all the preparation steps [1]. It also provides a flexible method in preparing semiconducting materials such as SiO_2, SnO_2, TiO_2 and many more for devices like resistors, electrodes and other components in electronic circuits [2]. In this work, screen-printing technique was employed to prepare TiO_2 layer onto ITO-covered glass substrate for use in solar cell and electrochromic window that are integrated in a single device [3]. TiO_2 has also been widely used in the pigment industry, catalysis, inorganic membranes, microelectronics and photocatalysis [4]. It is n-structure semiconductor since majority of charge carrier in it is electron. It exists in three different phases, namely, rutile, anatase and brookite. Rutile structure is the most stable phase at temperature between 25°C to 400°C, and displays tetragonal crystal structure. The crystal structure of brookite (TiO_2) is orthorhombic and is stable at temperature up to 625°C, whereas anatase crystal structure is tetragonal and exists at temperature up to 800°C.

Films made of semiconductor particles like TiO_2 fired at high temperature can provide nanoporous structure, which can be utilised as solar cell [5]. The film with high degree of porosity can accommodate more ions from the electrolyte material, like Li^+ [3] and this leads to the enhancement of photoelectrochemical reaction resulting in increase of device performance. In this paper, we report the preparation of TiO_2 film and their characterization of their phase structure, morphology and compositional properties using XRD, SEM and EDX respectively.

METHODOLOGY

Titanium dioxide, TiO_2 paste was purchased from Aldrich. The ITO-covered glass substrate undergone routine chemical cleaning using acetone, p-propanol and distilled water in sequence in ultrasonic bath. The cleaned substrate was then placed on the vacuum printing table. A small amount of the TiO_2 paste was put onto a clean mesh screen and then dispersed onto the ITO-covered glass substrate by a wiper of screen-printing device called squeegee. The vacuum pressure was 4 Bar. The screen-printing machine model used was ATMA TY-400 FA/T. The TiO_2 film was deposited 1 and 2 times by screen-printing a paste, consisting of TiO_2 particles and organic binder onto the substrate. The film was then tempered at 300°C, 350°C and 400°C for 30 minutes to burn out the organic parts and to achieve a highly porous structure. The tempered films were consequently quenched to room temperature.

XRD (X-ray diffraction) technique was performed on the film samples to study their phase structure. The model of equipment used was D8 Advance with the radiation source from CuK_α generated at energy of 40 kV and current of 40 mA, which emits a wavelength of 15.4 nm. The diffraction angle was from 10° to 60°. The sample grain size and the degree of porosity resulting from the different heat treatment were studied using SEM in the back-scattered electron (BSE) mode. These were obtainable from the image called micrograph taken at electron energy of 5 kV and 8 kV. The technique of EDX was used to identify the elemental composition of the samples. Spot-EDX (energy dispersive X-ray spectroscopy), done at energy of 30 kV provides the compositional information obtained from back-scattered electrons. In this work, SEM studies were reported in conjunction with EDX using model ESEM XL 30 tungsten.

RESULTS AND DISCUSSION

Figure 1 shows an example of the result of an EDX measurement on a sample annealed at 400 °C. The results showed the presence of Ti and O peaks together with C, O, Na, Mg, Si, K and C, which originated from the glass layer. Traces of Ti from ITO were also detected. This result is typical of all samples.

Figure 2 shows the SEM micrograph of TiO_2 films deposited once and annealed at 400°C. The average grain size was found to be around 6 μm, meanwhile, the one deposited once and fired at 300°C (Figure 3) has the average grain size of 10 μm. The size of the grain boundary of the films tempered at 400°C is bigger than that annealed at 300°C.

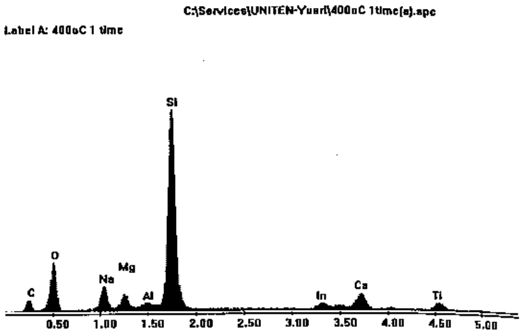

Figure 1. EDX spectrum for the sample annealed at 400°C

From both figures, the films are not homogenous since the grains sizes are not identical. It is expected that the grain size of the film prepared by screen-printing technique would be coarser than that prepared using other technique like electron beam evaporation, as screen-printing is one of the crude and rough techniques. Black regions represent titanium whereas white regions correspond to indium and tin [4]. From the two figures, the films are not porous as the pore size for the sample annealed at 400°C and 300°C are 1.5 μm and 2.5 μm respectively.

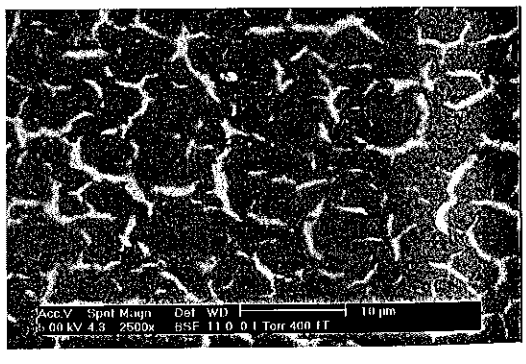

Figure 2. SEM micrograph for TiO_2 film deposited 1 time and annealed at 400°C

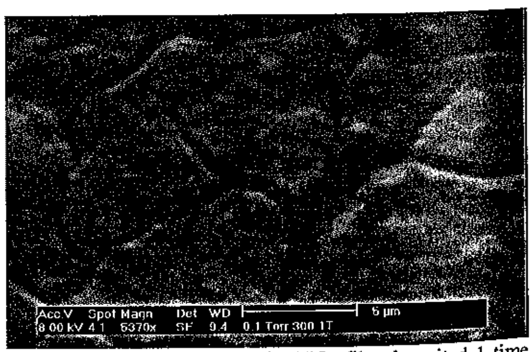

Figure 3. SEM micrograph for TiO_2 film deposited 1 time and annealed at 300°C

The results of XRD studies are shown in Figure 4, which show that both films deposited once and tempered at 300°C and 400°C have a low degree of crystallinity as the dominant peaks could not be observed. Nevertheless, the TiO_2 film with the anatase structure exists at a diffraction angle between 24° to 27° whereas the film with rutile structure exists at angle from 27° to 31°. They are consistent with reports in the literature [5] of XRD studies of TiO_2 deposited on alumina where rutile structure was found at the angle from 27 to 28°. There is a shift in diffraction angle for both phases of rutile and anatase. It agrees well with the theory that rutile structure is the most stable phase at temperature from room temperature to 400°C, and, exists in tetragonal crystal structure; this trend is similar to anatase structure. The peaks occur at the angle from 10° to 20° and after 30°C peaks are suspected to belong to ITO (indium tin oxide) layer. It is because x-ray of energy of 30 kV can penetrate ITO layer since TiO_2 film is quite thin with thickness of several μm. This can be observed in a diffractogram of ITO-covered glass substrates, shown in Figure 4.

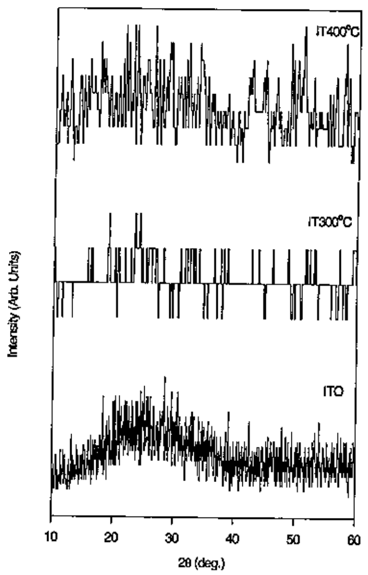

Figure 4. XRD diffractogram for ITO-covered glass substarate, TiO_2 film deposited 1 times and annealed at 300°C and 400°C

Figure 5 depicts the x-ray diffractogram of samples deposited once (lower trace) and those deposited twice and annealed (upper trace). It was found that the thicker TiO_2 films have a higher crystallinity degree. It may be due to the coming x-rays penetrating the same material layer of TiO_2. The peaks corresponding to anatase and rutile phase structure are still within the diffraction angle ranges from 20°C to 30°C and the peaks exist out of this range are suspected to belong to ITO-covered glass substrate. Also, from Figures 4 and 5 it can be inferred that the film deposited twice and annealed at 300°C has the highest crystallinity degree since its diffractogram has the lowest noise level and the sharpest peak.

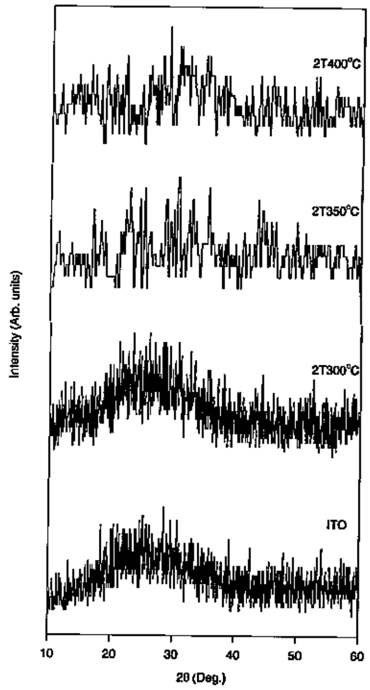

Figure 5. XRD diffractogram for ITO-covered glass substrate, TiO_2 film deposited 2 times and annealed at 300°C, 350°C and 400°C

CONCLUSIONS

Since the films are not homogeneous, porous and crystalline, further research need to be carried out to improve the film quality in order to optimize the performance of the solar cells and consequently electrochromic window.

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