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Microstructural investigation and SnO nanodefects in spray-pyrolyzed SnO_2 thin films

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ABSTRACT

Spray pyrolysis is one of the most cost-effective methods to prepare SnO_2 films due to its ability to deposit large uniform area, low fabrication cost, simplicity and low deposition temperature. Conventionally, scanning electron microscopy (SEM) and X-Ray Diffraction (XRD) are routinely used to investigate microstructure and crystal structure of the SnO_2 films. In the present study, the SnO_2 films were deposited by spray pyrolysis at 300, 400 and 500 °C and the microstructure of the 500 °C film was further examined by using transmission electron microscopy (TEM) and convergent beam electron diffraction (CBED). It was found that large grain-size vertically-aligned columnar SnO_2 grains were formed after a few layers of small grain-size randomly oriented SnO_2 grains. Moreover, CBED showed the presence of SnO nanodefects that had not been reported before and could not be detected by SEM or XRD.

1. Introduction

There have been extensive studies of microstructure of tin oxide (SnO_2) thin films because of their high electrical conductivity, high transparency in the visible solar spectrum, and high reflectivity in the infrared (IR) region [1–10]. Spray pyrolysis is one of the most cost-effective methods to prepare the SnO_2 films due to its ability to deposit large uniform area, low fabrication cost, simplicity and low deposition temperature. Spray pyrolysis is a chemical deposition technique in which fine droplets of a solution containing desired species are sprayed on a preheated substrate. Thermal decomposition takes place on the hot substrate, giving rise to a continuous film. Compared to chemical vapor deposition (CVD) where the precursors of a reaction must be first vaporized, then mixed and directed onto a hot substrate surface, spray pyrolysis also involves film growth from the vapor phase. Whether or not the pyrolysis process can be classified as CVD depends on whether the liquid droplets vaporize before reaching the substrate or react on it after splashing [11]. Preheating of the sprayed droplets is used to ensure the vaporization of the reactants before they undergo a heterogeneous reaction at the substrate [12]. However, although contact of the liquid droplets with the substrate surface is known to be detrimental, it cannot be avoided completely. Addition of non-aqueous solvents to the solution can be used to increase the amount of vapor produced and hence increase the efficiency [4]. Structural characterization of the spray-pyrolyzed SnO_2 films has so far been investigated mostly by scanning electron microscopy (SEM) and X-Ray Diffraction [7,8,10–13]. It was commonly observed that the microstructure of the SnO_2 films depended strongly on the deposition temperatures used. Korotcenkov et al. [14] further investigated the spray-pyrolyzed SnO_2 films deposited on silicon substrates and reported the evolution of the crystallographic orientation of the films with variation of the pyrolysis temperature using SEM, XRD and high resolution transmission electron microscopy (HRTEM). Faceting of the SnO_2 nanocrystallites was observed to be formed by different crystallographic planes of which the dominant planes depended on deposition temperature and film thickness. This study further investigates morphology of the SnO_2 films using transmission electron microscopy (TEM) and convergent beam electron diffraction (CBED) in addition to SEM and XRD in order to gain an in-depth understanding of the SnO_2 film deposition by a low-cost non-vacuum spray-pyrolysis technique.

2. Experimental

In this investigation, the SnO_2 films were deposited on heated soda-lime glass substrates using spray pyrolysis with the aerosol produced by ultrasonic atomization [13]. A solution of $SnCl_2$ in a mixed solvent of 90% methanol and 10% deionized water was used as a precursor. Compressed air was used as the carrier gas. The SnO_2 films were deposited at temperatures of 300 °C, 400 °C, and 500 °C, respectively. The precursor solution was atomized into fine droplets and carried upwards to a heated substrate. Spray pyrolysis was then carried out for 30 minutes to form each film, after which the substrate was allowed to cool to room temperature before further analysis. Morphologies of the SnO_2 films were investigated using field emission

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scanning electron microscopy (SEM) (JEOL JSM-6301 F) and transmission electron microscopy (TEM) (JEOL JEM-2010 operated at 200 kV). The cross-sectional TEM samples were prepared using a focused ion beam (FIB) technique. The crystal structures of the SnO_2 films were studied using a Rigaku TTRAX III X-ray diffractometer (XRD) using CuK_α radiation operated at 50 kV, 300 mA.

3. Results and Discussion

Figs. 1 and 2 show SEM micrographs and XRD patterns from SnO_2 films deposited at 300, 400 and 500 °C. The SnO_2 film deposited at 300 °C was found to be amorphous with small circular surface grains. The SnO_2 film deposited at 400 °C was found to be polycrystalline with various surface grain shapes and sizes. The SnO_2 film deposited at 500 °C contains the largest average grain size (Fig. 1(c)) and the highest crystallinity (the highest peak intensity in Fig. 2). Although being the most crystallized, surface porous microstructure was observed on the surface of this sample. Porous microstructure for the whole film thickness would be undesirable. However, cross-section images investigated by SEM showed that the large grain-size SnO_2 films were dense and resulted in good electrical performance [7,13].

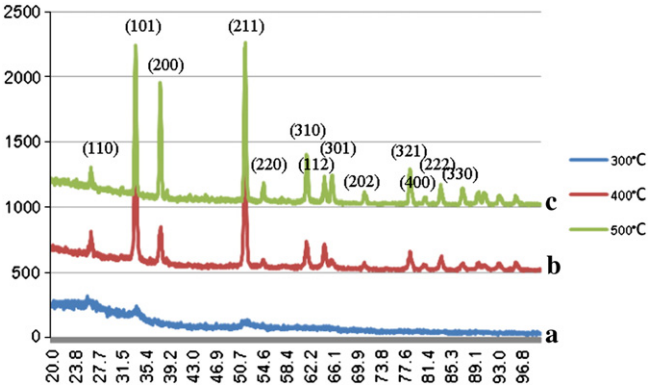

Fig. 2. X-ray diffraction patterns taken from the spray-pyrolyzed SnO_2 films deposited at (a) 300 °C, (b) 400 °C and (c) 500 °C, respectively.

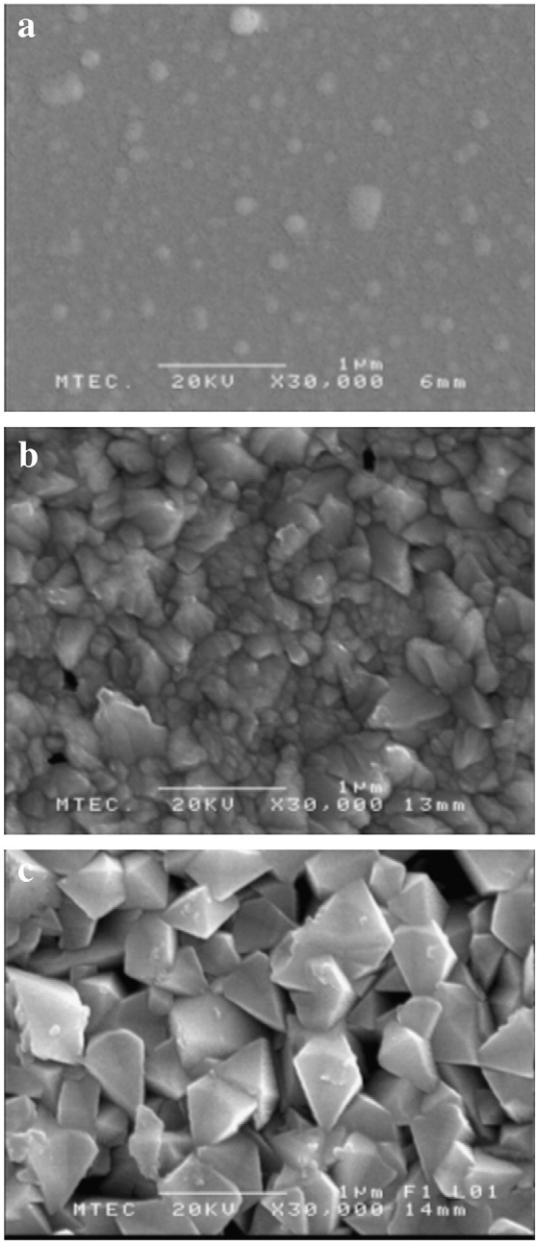

Fig. 1. SEM micrographs of the spray-pyrolyzed SnO_2 films deposited at (a) 300 °C, (b) 400 °C and (c) 500 °C, respectively.

Fig. 3 shows bright-field TEM micrographs and diffraction patterns taken from different areas in the SnO_2 film deposited at 500 °C. Fig. 3 (a) shows a low-magnification bright-field TEM micrograph to observe overall film thickness of ~3.5 microns (underneath the surface of the film shown in Fig. 1 (c)). The buffer zone is observed above the interface between the SnO_2 film and the glass substrate. Above the buffer zone, a ~500 nm-thick layer consisting of randomly oriented columnar grains (zone I in Fig. 3 (b)) was formed. The corresponding diffraction pattern of zone I suggests polycrystalline SnO_2 layer with a few preferred orientations. The next layer was formed (zone II in Fig. 3 (b)) consisting of small equiaxed nuclei firstly formed at the interface between layer I and II. Then, columnar growth similar to that reported by Korotcenkov et al. [14] is observed with a flatter surface, an average grain size of ~100 nm and the thickness of ~250 nm. However, the SnO_2 film investigated by Korotcenkov et al. [14] was grown on Si substrate which is much smoother than glass substrate used in this study. The results suggest that, when enough precursors and time were given, the crystals in the SnO_2 films prepared by spray-pysolysis on glass substrates would self-align to yield an optimum thickness for each zone. Moreover, the grains in the zone away from the substrate were found to be single crystal-like, i.e. large long columnar grains resulting in spotty electron diffraction pattern. With 30 minutes allowed for the SnO_2 film deposition at 500 °C, the last layer of thickness of more than 2.5 microns was obtained (zone III and IV in Fig. 3 (b) and (c), respectively). TEM micrographs and electron diffraction patterns (Fig. 3) show that after the buffer zone, the layer of rough polycrystalline SnO_2 with preferred orientations (zone I) was formed and followed by interface equiaxed grains and randomly oriented columnar fine grains in the polycrystalline SnO_2 (zone II) layer. Then, the next layer started with interface equiaxed grains followed by columnar growth with vertical grain boundaries (indicated by horizontal streaks in zone III diffraction pattern). Zone IV diffraction pattern indicates that the top region of this layer consists of large columnar grains aligning themselves vertically. Although there are fine equiaxed nuclei formed at the beginning of each layer growth, the results suggest that the SnO_2 crystals can finally arrange themselves to provide large columnar grains with vertical grain boundaries. Moreover, this study shows that vapor phase deposition was fully achieved at the 500 °C deposition temperature [15]. Compared to other non-vacuum and low-cost SnO_2 preparation techniques, the high crystal quality observed in this study is believed to be beneficial. For example, the high crystal quality of the top region on the SnO_2 film has a

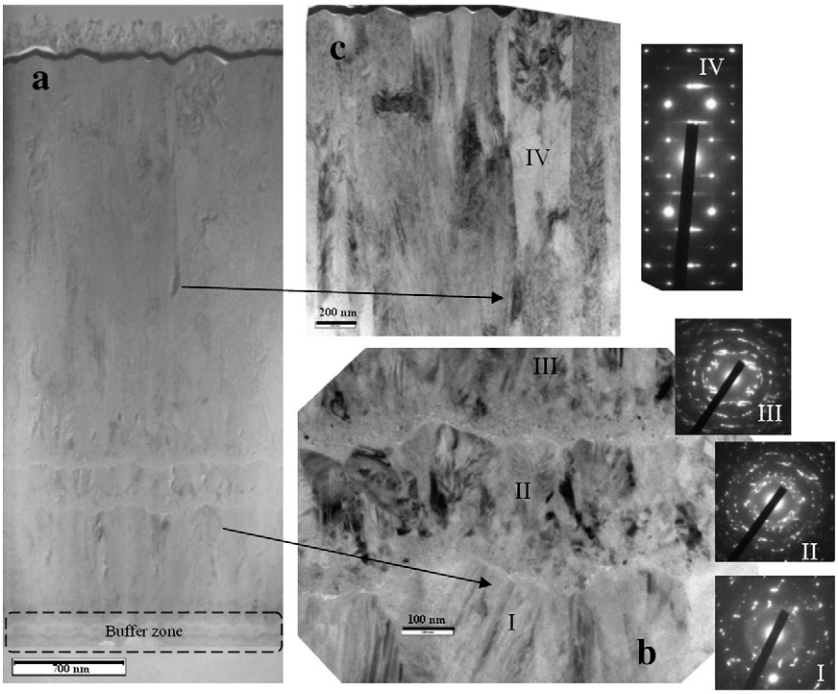

Fig. 3. Bright field TEM micrographs of different zones in the spray-pyrolyzed SnO_2 thin film deposited at 500 °C and their corresponding diffraction patterns. (a) The full film thickness, (b) a magnified area from (a) as indicated by the bottom arrow, and (c) another magnified area from (a) as indicated by the top arrow.

potential usage as a low-cost high-quality substrate for other lattice matching systems which requires further investigations.

In the case of the undoped SnO_2 films, it is well known that the electrical properties of the films depend on the quality of the films, stoichiometry and structural properties [1–10,12–15]. Phases present in the top area of the film were, thus, investigated using convergent beam electron diffraction (CBED). Fig. 4 shows a bright-field TEM image taken from a columnar grain in the top area of the SnO_2 film with inset CBED patterns. A CBED pattern from a relatively defect free area (marked 1) is shown in Fig. 4 (a). This pattern corresponds to [001] SnO_2 and is typical of most of the grains in the film. The CBED pattern in Fig. 4 (b) comes from a defect area (marked 2) and is found to correspond to [021] SnO. SnO was, thus, found to be present in the deposited undoped SnO_2 films even though it was present at a concentration too low to be detected in the X-ray diffraction patterns (Fig. 2).

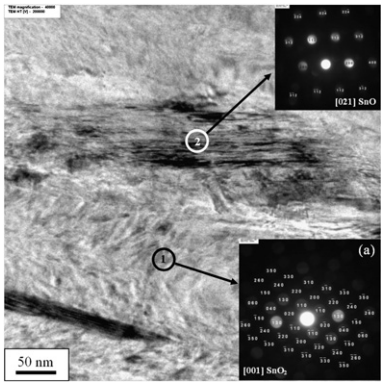

Fig. 4. Bright-field TEM image of the SnO_2 columnar crystals deposited at 500 °C with insets (a) CBED pattern taken from area 1, indexed as [001] SnO_2 and (b) CBED pattern from area 2, indexed as [021] SnO.

4. Conclusion

It has been shown that the spray-pyrolyzed SnO_2 film deposited at 500 °C for 30 minutes on the glass substrate consists of a number of distinct zones. In this study, 5 main zones were observed, i.e. buffer zone above the interface between the SnO_2 film and the glass substrate, zone I as the ~500 nm-thick polycrystalline SnO_2 layer with a few preferred orientations, zone II as the ~250 nm-thick randomly-oriented polycrystalline SnO_2 layer, zone III as the bottom part of the top layer consisting of interface equiaxed grains and the beginning of the vertical columnar grains and, finally, zone IV as top part of the top layer consisting of the high quality vertically oriented columnar grains. However, SnO nanodefects were also found by CBED to be present in the top part of the high quality SnO_2 film. These nanodefects could neither be detected by SEM nor XRD.

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