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Surface modification of tin oxide ultrafine particle thin films

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Abstract

Tin dioxide ultrafine particle thin films were deposited by the dc gas discharge activating reaction evaporation technique over four different substrates: fused quartz, monocrystalline Si, microcrystalline glass, and commercial glass. Changes in both the morphology and crystallinity of the films were studied by scanning tunneling microscopy and X-ray diffraction, respectively, as a function of different substrates and deposition conditions. The results showed that the morphology and crystallinity strongly depended on not only the nature of the substrate, but also the deposition conditions. The interesting surface "structural unit" was obtained by using a higher dc gas discharge voltage under relative low oxygen partial pressure ($V_d \geqslant -1100$ V and $P(O_2) = 5.0$ Pa). It suggests that a high discharge voltage was necessary to obtain the films with rich crystallinity and/or special microstructure. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: A. Oxides; A. Thin films; B. Vapor deposition; C. Scanning tunneling microscopy; D. Microstructure

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1. Introduction

The structural and morphological characteristic of polycrystalline tin oxide thin films are of great importance in various applications such as chemical sensors, solar cells, and optoelectronic devices [1–3]. Generally, the gas sensing properties of tin oxide materials are explained by the surface reaction between chemisorbed oxygen and sensing gases [4,5]. Consequently, its sensitivity as a gas sensing material is dependent on the grain size, surface morphology, and internal porosity [6,7]. Therefore, the morphology, microstructures, phase, and chemical composition are commonly known to be the most important factors in gas sensing properties due to their relationship to specific electrical properties of tin oxide films.

In recent years, the trend has been to study the SnO_2 material in detail and to enhance its performance by using all sorts of methods, such as through surface modification of the sensor [8–13]. It is noted that the gas sensitivity is strongly dependent on the grain growth of SnO_2 thin films. The results show that the grain growth corresponds to an activation behavior. Much of this activity focuses on grain growth kinetics of SnO_2 thin films. Therefore, precise control of the grain growth is very attractive in the preparation of SnO_2 thin films. In earlier work [14–20], it was realized that the electrical properties of the films strongly depend on the crystal orientation properties, which in turn depend on the deposition conditions.

In this study, the morphologies and the crystallinity of tin oxide ultrafine particle thin films (UFP) were investigated by using X-ray diffraction (XRD) and scanning tunneling microscopy (STM), respectively. In particular, we noticed that not only the nature of the substrates used for the deposition, but also the extreme parameters seem to play an important role in obtaining rich crystallinity and/or some other specific microstructure UFP thin films.

2. Experimental

The deposition system and the procedure of the dc gas discharge reaction evaporation device has been described previously [20]. The samples used in this paper were prepared as follows. The vacuum chamber was pumped down to 10^{-3} Pa and the temperature of the sample substrates was raised to 300°C. Oxygen was then introduced into the vacuum chamber. The oxygen partial pressure was kept at 5–6 Pa. A dc discharge voltage of 950 to about −1100 V was applied to the ring electrode. Thus, a gas discharge region, in which the oxygen molecules were activated, was produced between the substrates and the top of the shielding can. Finally, the evaporation temperature was slowly raised to evaporate tin powder (99.5%), and tin atoms entered the discharge region and reacted with activated oxygen molecules, and then deposited together on substrates. The deposition lasted for 15–20 min. The thickness of the films is ~300–500 nm.

The crystal structure was evaluated by X-ray diffraction (Rigaku, DMAX/γB). Scanning tunneling microscopy (CSTM-9100, Peking University) was employed to characterize microstructure and morphology of the films in the constant current mode, (tunneling current I_t = 0.64 nA, bias voltage V_{bias} = −0.789 to about −1.000 V) in air at room temperature. The tips used were produced from a 0.2 mm tungsten wire (99.99%) by a routine electrochemical etch, in an aqueous 1.9 M NaOH solution.

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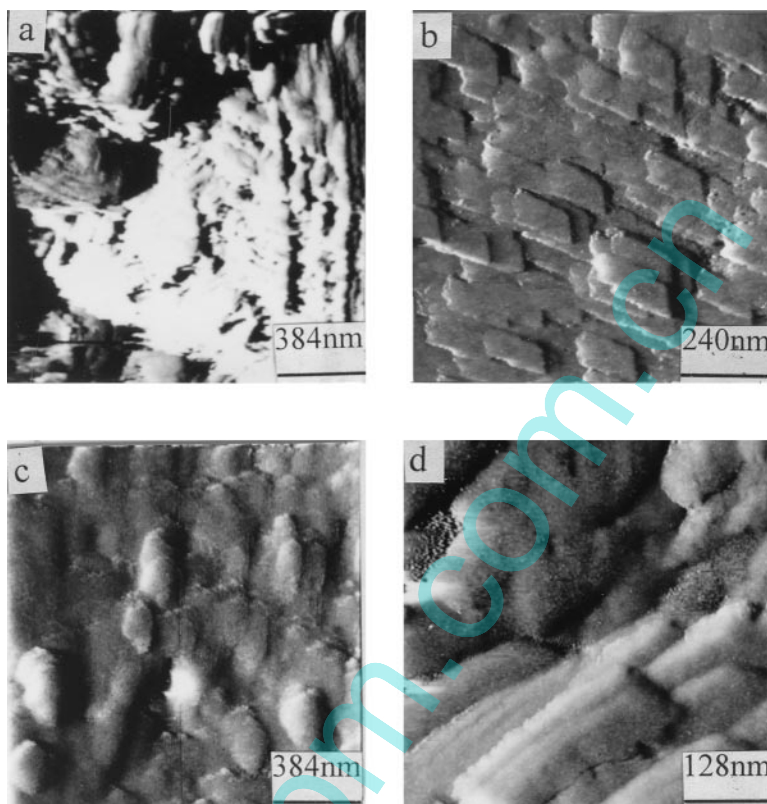

Fig. 1. STM images of SnO_2 UFP thin films deposited by using relative lower dc gas discharge voltage and oxygen partial pressure (V_d = −950 V, $P(O_2)$ = 5.0 Pa) on different substrates of (a) fused quartz, (b) monocrystalline Si, (c) microcrystalline glass, and (d) commercial glass.

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3. Results and discussion

The STM images, as shown in Figs. 1 and 2, revealed that both the nature of the substrates and the deposition parameters gave rise to several effects on the morphological changes of the films. Firstly, the influence of the substrates was evident, as shown in Fig. 1. It was noted that microstructures of the films on fused quartz, microcrystalline glass, and commercial glass were somewhat irregular in configuration with the grain boundary surfaces, which were found to be in close-packed configuration, while the film on Si(111) was very regular in configuration. Secondly, as shown in Fig. 2, the gas discharge voltage seemed to have a stronger influence on the structural characteristics of the thin films, because the modifications in the layers occurred only when higher gas discharge voltage (1100 V) was used. No difference in surface morphology of the films deposited on Si(111) was observed as the discharge voltage increased from 950 to 1100 V or more, as shown in Figs. 1(b) and 2(b). However, a very interesting result was that the shape of the crystallite could be greatly changed on the commercial glass substrate when the parameters were in extreme values, as shown in Figs. 1(d) and 2(d). It was noted that significant "structural unit" formation was

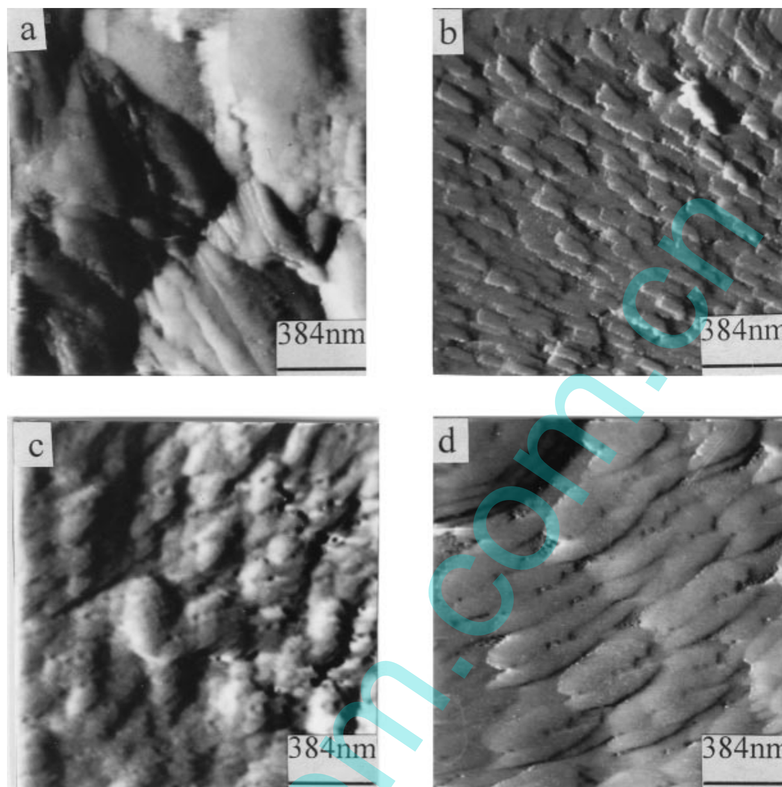

Fig. 2. STM images of SnO_2 UFP thin films deposited by using higher dc gas discharge voltage (V_d = −1100 V, $P(O_2)$ = 5.0 Pa) on different substrates of (a) fused quartz, (b) monocrystalline Si, (c) microcrystalline glass, and (d) commercial glass.

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evident. The surface morphology of the grains in this view appeared to be quite different from that in Fig. 1(d). During microstructural change, realignment of grains into a preferred orientation and/or grain growth was observed, of which the degree depended on a very high discharge voltage under a lower oxygen partial pressure. The STM images shown in Figs. 1(c) and 2(c) indicated obvious changes in grain structure and morphology at the high discharge voltage parameters on microcrystalline glass, and a significant void formation was present at the grain interfaces compared to that at the low discharge voltage parameters.

Fig. 3 showed the electron diffraction patterns of the typical SnO_2 UFP films, corresponding to the cases in Figs. 1 and 2. A strong XRD peak attributed to the (110) plane of cassiterite and weak XRD peaks corresponding to the (101), (211), and (220) planes were obtained. The spectrums confirmed that the films were polycrystalline with the tetragonal rutile structure.

For comparison, the XRD patterns from the lower discharge voltage were also shown. Changes in the diffraction peak intensity were evident. Further examination of the data in our experiment indicated that as the discharge voltage increased from 950 to 1100 V, the films underwent the phase transformation from SnO to SnO_2, and the crystallinity changed from poor to rich.

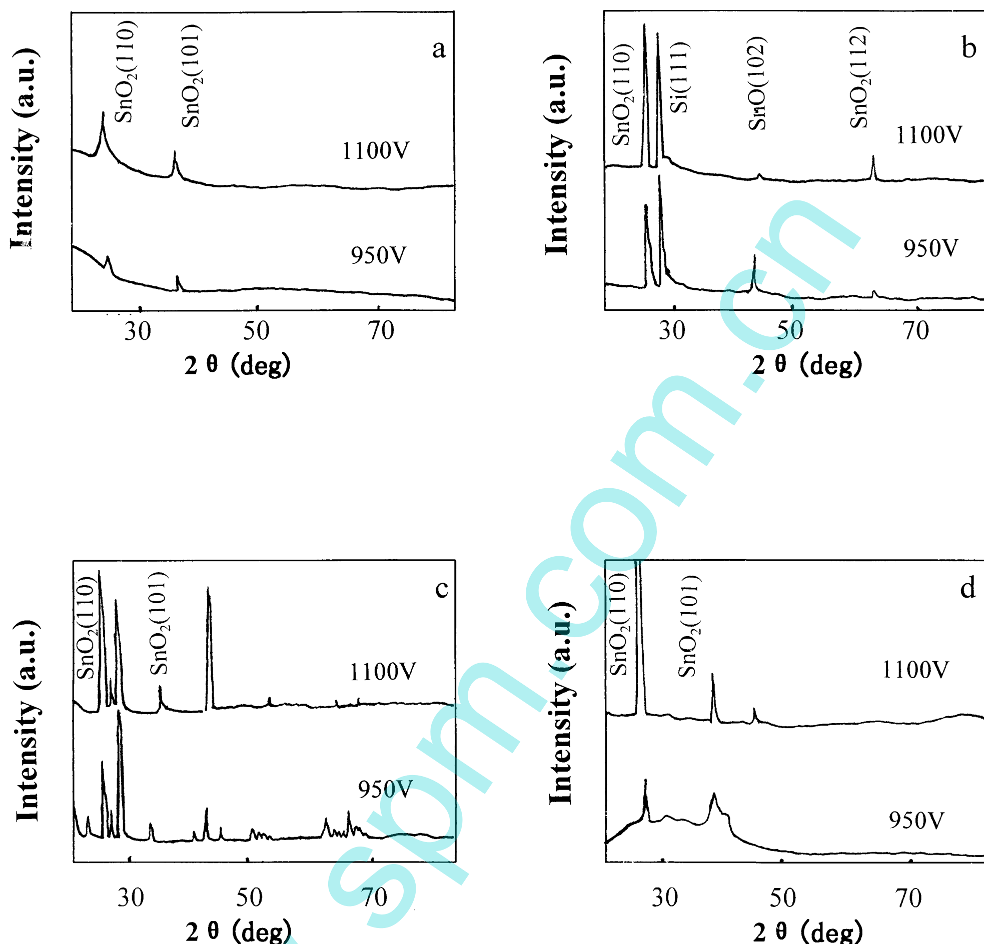

Fig. 3. XRD patterns of SnO_2 UFP thin films, corresponding to the cases in Figs. 1 and 2: (a) fused quartz, (b) monocrystalline Si, (c) microcrystalline glass, and (d) commercial glass.

For all polycrystalline samples, tin dioxide was the main component of the films as discharge voltage increased up to 950 V. For the sample deposited on microcrystalline glass substrate many extra peaks were detected, which we associated with the substrate. All polycrystalline films showed a preferential orientation in the (110) and (101) direction, except the sample deposited on Si(111) substrate.

We did observe during the experiments that the degree of the crystallinity of the films was very dependent on the nature of the substrates. Commonly, the use of monocrystalline Si and microcrystalline glass substrates easily allows a better degree of crystallinity under the same conditions, as well as the lowest amorphous–polycrystalline transition temperature. We found that the crystallinity of the films depended not only on the nature of the substrate, but on the extreme values of the gas discharge voltage under relative lower oxygen partial pressure (V_d = −1100 to about −1200 V and $P(O_2)$ = 5.0 Pa). According to Chopra [21] and Poate et al. [22], the type of texture obtained for a given material in the form of thin film

is related to its crystalline structure, which determines the crystallite shape compatible with the lowest interfacial free energy. Fantini et al. [23] proposed that the textures can be modified by the deposition parameters, which influence the atomic mobility, as well as other factors, such as the nature and smoothness of the substrate surface. Other reports [24,25] on preferred orientation mentioned that each starting compound leads to its own characteristic oriented growth, independently of growth conditions. The results from those reports indicated that the oriented growth is affected not only by substrate temperature and supersaturation, but also by the structure of the starting compounds. However, the present results strongly suggest that the preferred orientation can be controlled by not only the nature of the substrate, but also the extreme deposition conditions.

In our experimental procedure, if a very high discharge voltage is applied to the ring electrode, the plasma region will offer enough energy to activate the oxygen molecules and tin atoms. Therefore, the well-activated tin atoms have a chance to react with well-activated oxygen molecules and then selectively absorb and/or combine nuclei, and grow with preferred orientation basis of the lowest surface free energy. In addition, our results showed that once the discharge voltage was fixed at less than 1100 V, the microstructural change of the UFP films due to the other operating conditions such as oxygen partial pressure was not so noticeable. Therefore, this result further confirmed that the "structural unit" mainly results from a very high discharge voltage. Additional work is needed to clarify the influence of the extreme deposition conditions on the microstructure variation found in this experiment.

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