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Investigation on Defects of Sb Doped SnO_2 Thin Films by Positron Annihilation

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Undoped and Sb doped tin oxide thin films were fabricated by the dip-coating technique through a propylene oxide assisted sol-gel method. Atomic force microscope measurements reveal that the grain size increased after being calcined at higher temperature; while increasing the dopant content leads to a reduction in grain size and a corresponding increase in the concentration of grain boundaries. Positron annihilation spectroscopy analysis shows the defects are reduced with increasing Sb content to 5 %; however, further increasing the doping level to 10 % introduces more defects to the films. At all doping levels, the defects in Sb doped tin oxide films decreases significantly upon elevating the calcination temperature.

1. Introduction

Interest in tin oxide thin films has increased in recent years due to their application to transparent oxide semiconductors, solar cell electrodes and gas sensors. Research shows that doping SnO_2 with elements such as F, Mn, and Sb could further improve the working performance, such as higher conductivity, better optical transmittance and ferromagnetism [1–3]. It is generally accepted that defects and doping are important in determining the relative electrical and optical properties of alien elements in doped SnO_2. Therefore, an investigation on defects in SnO_2 based films could lead to an improvement in performance as a transparent conductive oxide material.

The nondestructive positron annihilation technique is extensively utilized to investigate defects in materials [4,5]. In the present work, SnO_2 thin films with various Sb doping levels were fabricated using the sol-gel method though a dip-coating procedure. Doppler broadening of annihilation radiation (DBAR) spectroscopy and variable energy positron annihilation lifetime spectroscopy (VEPLS) based on a pulsed positron beam as well as atomic force microscopy (AFM) were used to study the synthesised Sb doped SnO_2 (ATO) thin films.

2. Experiment

2.1 Sample preparation

Undoped and Sb doped SnO_2 thin films were synthesised according to the previously described procedure [6,7]. Appropriate amounts of $SnCl_4{\cdot}5H_2O$ and $SbCl_3$ in 37 wt% HCl were dissolved stoichiometrically in ethanol, then the precursor sols were prepared by adding propylene oxide into the mixed solutions. Silicon (110) wafers, precedentially subjected to hydrophilic surface treatment, were used as film substrates. In addition to undoped films, Sb doped tin oxide thin films were prepared with various Sb/Sn molar ratios of 2 mol%, 5 mol% and 10 mol%. All films were pre-dried at 100 °C for 1 h, and were successively calcined at 400 °C, 600 °C and 800 °C in air for 2 h.

2.2 Characterization of ATO films

DBAR spectra were recorded by a high purity Ge detector using the slow positron beam at Wuhan University. The line shape parameter *S* was calculated as the ratio of the central region of the 511 keV peak to the total area, and the wing parameter *W* was defined as the ratio of wing regions to the total area. The *S* parameter concerns the annihilation of positrons with low momentum electrons, and the *W* parameter is associated with positron annihilation of higher momentum electrons. Variation of the *S* and the *W* parameters implies a change in the physicochemical environment which is closely related to the defect species and chemical elements around the positron localization sites [8]. Positron lifetime spectra were measured at a fixed incident positron energy of 1.25 keV by VEPLS in AIST, Japan. The surface morphology of the films were examined via tapping mode AFM (SPM-9500J3, Shimadzu). The thicknesses of the calcined films were determined to be around 20 nm by spectroscopic ellipsometry.

3. Results and discussion

3.1 AFM characteristics for the ATO films

Figure 1 shows the surface morphologies of the undoped tin oxide films annealed at (a) 400 °C, (b) 600 °C, (c) 800 °C and 2 % Sb doped SnO_2 film calcined at (d) 400 °C, (e) 600 °C and (f) 800 °C, respectively. The obtained images indicate that the grain size increases from ~42 nm for the film

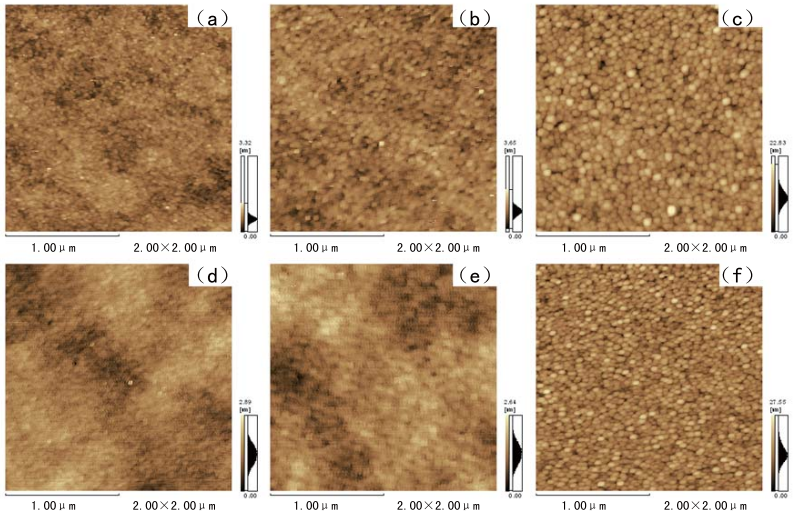

Fig. 1. surface morphologies of undoped tin oxide films annealed at (a) 400 °C, (b) 600 °C, (c) 800 °C and 2 % Sb doped SnO_2 film calcined at (d) 400 °C, (e) 600 °C and (f) 800 °C, respectively.

calcined at 400 °C to ~70 nm for the film calcined at 800 °C, meaning the diminishment of grain boundaries [9]. The result signifies that the defects are reduced, accompanied with the disappearance of some grain boundaries upon calcination. For the doped thin films, the grain size also increases with increasing the calcination temperature. A lower concentration of grain boundaries implies that the films are less disordered. Comparing to the undoped films, it is noted that the grain size of the particles decreases in SnO_2 films doped by 2 mol% Sb, demonstrating an increase in the grain boundary concentration after doping with Sb. Doping with alien atoms is expected to introduce more disorder to the film. Thermal treatment plays a critical role in reducing the defects as discussed in the following section.

3.2 Positron annihilation characteristics of the ATO films

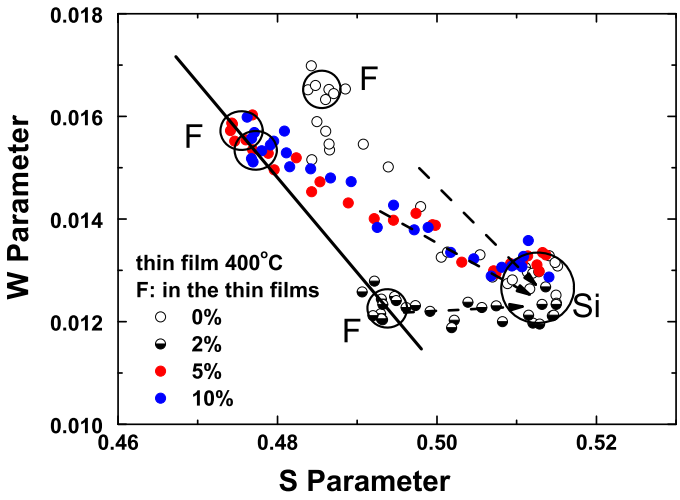

Fig. 2. *S*–*W* plot for ATO films calcined at 400 °C. Dash arrow lines indicate the increase of incident positron energy.

Figure 2 depicts the *S* parameter plotted against the *W* parameter for both the undoped and Sb doped tin oxide thin films calcined at 400 °C. For all the films, S increases and W decreases gradually with increasing incident positron energy from the bulk region F in thin films to the Si, which represents the positron annihilation in the bulk of the Si substrate. The positron stopping fraction varies with increasing the incident positron energy. For the ATO films calcined at 400 °C, the values of (*S*,*W*) in the Sb-doped films, namely in F regions, are located on a straight line (shown as a solid line in Fig. 2), while the values of (*S*,*W*) in the undoped film significantly deviate from this line. This indicates that positrons sensitively detect the Sb atoms in the tin oxide films. The results suggest that the doped Sb atoms may be associated with vacancy clusters as well as grain boundaries existing in the SnO_2 films. Furthermore the obvious difference in the *S* parameter between the 2 % and 5 % doped films implies either a change in the type of defects at the first stage of the Sb doping into the film or that excessive amounts of doped Sb reduces the positron annihilation with the Sb atoms associated with the defects.

For all samples calcined at 800 °C, the *S* parameter plotted against the *W* parameter for both the undoped and Sb doped tin oxide thin films is shown in Fig. 3. The variation of the *S* parameter versus the *W* parameter in these films can be fitted by a straight line, which reflects the change in the annihilation sites of positrons with varying Sb content. The gradual increase in *S* and decrease in *W* from the undoped film to the 10 % Sb doped film calcined at 800 °C might result from the increasing probability of positrons annihilating with Sb. Furthermore, the change in both *S* and *W* from 5 % to 10 % Sb doped film calcined at 800 °C is very small, this probably indicates that a homogeneous stable structure is formed after the thermal treatment. As reported previously [7], the defects, including oxygen vacancies, are reduced when calcining at higher temperature in air, the grain boundaries are eliminated, and the Sb dopants probably become substitution atoms at the Sn positions, namely the possible formation of a Sb_{Sn} structure.

Figure 4 displays the mean positron lifetime τ_m of the ATO films with various Sb contents calcined at (a) 400 °C, (b) 600 °C and (c) 800 °C, respectively. Two positron lifetime components (τ_1

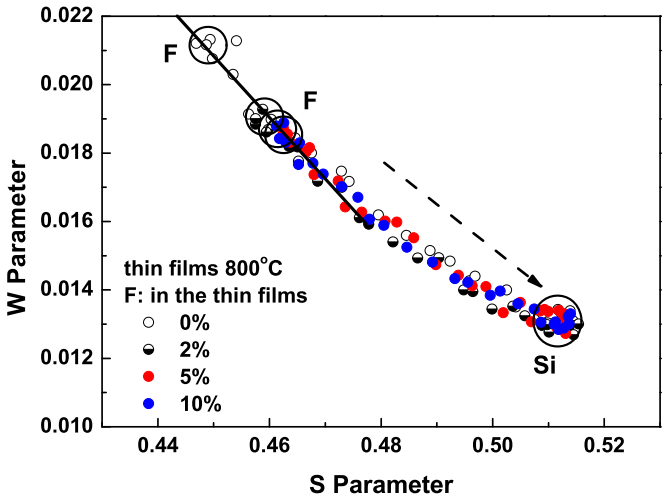

Fig. 3. *S*–*W* plot for the ATO films calcined at 800 °C. The dash arrow line indicates the increase of incident positron energy.

and τ_2) were derived from the measured VEPLS. The mean positron lifetime (τ_m) is determined by $\tau_m = (I_1\tau_1 + I_2\tau_2)/(I_1 + I_2)$ [10, 11]. Initially, for all films calcined at 400 °C, the mean positron lifetime decreases with increasing dopant concentration, from 399 ps in undoped SnO_2 films to 375 ps in 5 % Sb doped films with increasing the dopant content. However, at even higher concentrations the mean positron lifetime increases, with a value of 423 ps for 10 % Sb doped films. Addition of a small amount of Sb (less than 5 %) to the films may result in a decline in the vacancy-type defects, while the positrons substantially annihilate with the higher momentum electrons of the Sb atoms, giving rise to the higher *S* parameter. While an excessive doping level of 10 % introduces more defects/grain boundaries to the films. At a relatively low calcination temperature of 400 °C, the doped Sb atoms mainly exist in the substitutional and/or the interstitial sites, and the heavy doping level of 10 % might cause more disorder in the films, resulting in an increase of τ_m. Meanwhile, for the films calcined at 600 °C, the τ_m firstly increases from 342 ps in undoped film to 362 ps in 2 % Sb doped film, and then slightly reduces to 355 ps in 5 % Sb doped film and remains almost the same for 10 % Sb doped film. For films calcined at 800 °C, τ_m increases from 294 ps in the undoped film to a platform at 339 ps in all Sb doped SnO_2 films due to the formation of a stable structure at a higher temperature.

The mean positron lifetime decreases for all films with increasing calcination temperature. Nevertheless, for the undoped film, τ_m significantly declines with increasing calcination temperature from 400 °C to 800 °C, implying that it is easier to reduce defects during the thermal treatment. And for the 2 % and 5 % ATO films, the decrease in τ_m is not prominent with increasing calcination temperature, meaning that the growth of grains is suppressed with doping and the defects are much more difficult to eliminate upon calcination compared with the undoped films. This result is consistent with the AFM observations. For the 10 % ATO film, τ_m declines distinctively upon elevating the calcination temperature from 400 °C to 600 °C, and then it remains constant upon further calcination, indicating a reduction in the external defects caused by excessive dopant.

4. Conclusion

In summary, undoped and antimony doped tin oxide thin films were synthesized using a sol-gel method. The effects of the antimony concentration and calcination temperature on the structure and

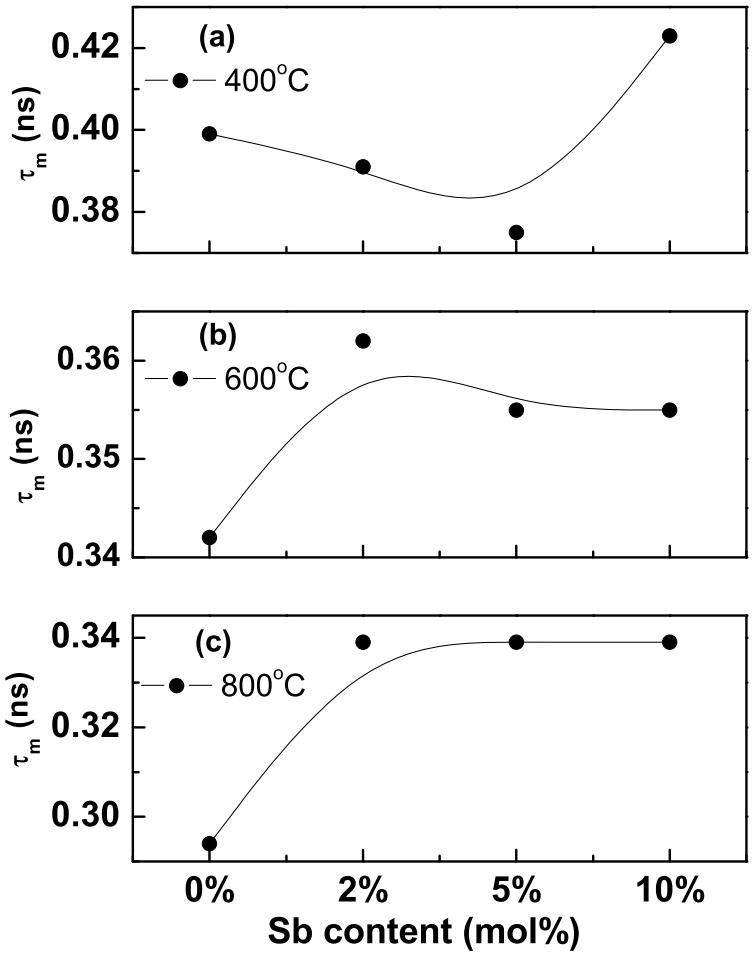

Fig. 4. Mean positron lifetime (τ_m) as a function of Sb doping level for the ATO films calcined at (a) 400 °C, (b) 600 °C and (c) 800 °C, respectively. The lines are guides to the eye.

defects of antimony-doped tin oxide films were studied by AFM, DBAR and VEPLS. The grain size increased and the grain boundaries of the films were reduced upon calcination at higher temperatures. For undoped films, defects including oxygen vacancies were gradually reduced upon calcination. Even though a heavier doping level introduced more defects to the Sb doped thin films, the defects were reduced with increasing calcination temperature. A higher calcination temperature was favorable to eliminate defects.

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