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A study on phase transformation of SnO_x thin films prepared by reactive magnetron sputtering

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ABSTRACT

In the paper, SnO_x thin films were deposited by reactive magnetron sputtering from a tin target in O_2 containing working gas. The evolution from Sn-containing SnO to tetravalent SnO_2 films was investigated. The films could be classified into three groups according to their optical band gaps, which are $E_g < 2.5$ eV, $E_g = 3.0$–3.3 eV and $E_g > 3.7$ eV. The electric measurements show that high conductivity can be obtained much easier in SnO_2 than in SnO films. A high electron mobility of 15.7 $cm^2 V^{-1} s^{-1}$, a carrier concentration of 1.43×10^{20} cm^{-3} and a resistivity of 2.8×10^{-3} Ω cm have been achieved in amorphous SnO_2 films. Films with the optical band gap of 3.0–3.3 eV remain amorphous though the substrate temperature is as high as 300 °C, which implies that °btaining high mobility in p-type SnO is more challenging in contrast to n-type SnO_2 films.

1. Introduction

Both tin oxide (SnO_2) and tin monoxide (SnO) are important oxide semiconductors, which show natural n-type and p-type conduction respectively. SnO_2 has been widely studied and utilized as gas sensors [1], transparent anodes of solar cells [2], and channel layers of thin film transistors (TFTs) [3,4]. Recently, SnO has attracted considerable interests for its potential perspective to be used as the semiconductor layer in high mobility p-type oxide TFTs [5–9] because of its Sn 5s and O 2p orbits derived VBM that weakens the localization of O 2p orbits [6,9,10]. SnO-based TFTs have been reported a record field-effect mobility of 6.75 $cm^2 V^{-1} s^{-1}$ by Jesus A. Caraveo-Frescas [7].

The recently promising achievements in SnO-based TFTs open the interests in transparent CMOS, in which both high performance p-type and n-type TFTs are required. Many works have proposed varieties of n-type oxide semiconductors to complement nature p-type SnO. Hosono has reported bipolar conduction in SnO [11]. They realized n-type conduction in SnO by doping Sb. Other n-type oxide semiconductors, such as In_2O_3 [12] and IGZO (Indium–Gallium–Zinc–Oxide) [13] have also been utilized. Furthermore, SnO_2 is also promising because of its processing compatibility with a popular reactive sputtering method utilized to deposit SnO thin film. By changing O_2 content in the working gas, n-type SnO_2 and p-type SnO can be obtained, respectively [14].

Many present works intended to obtain pure SnO [6,7,15] or SnO_2 [15] thin films by reactive sputtering. Thus the intermediate process of phase transformation from SnO to SnO_2 which contain the mixture of the two oxides has been ignored. However, understanding the mixture is significant because phase impurity always challenges the control of film performances. The influences of phase impurity on the crystallization and electrical properties of the SnO_x films have not been revealed sufficiently as well. This paper will discuss the transformation from Sn-containing SnO thin films to SnO_2 thin films as well as the essential factors that impact the obtained SnOx thin films. The different influence of phase impurity and films crystallinity on SnO and SnO_2 films will also be discussed.

2. Experimental methods

SnO_x films were deposited on glass substrates by reactive mf (40 kHz) magnetron sputtering from a high purity (99.99%) tin target. The base pressure of the sputtering chamber was 2.0×10^{-3} Pa. The working pressure was 0.5 Pa. The working gas was a mixture of high purity (99.999%) O_2 and Ar. The flow rate ratio of $O_2/(O_2+Ar)$ (which will be written for short as O_2 ratio in the fallowing parts) varies from 20.0% to 31.7%. In order to clarify the influence on the crystallinity of SnO_x, the substrate temperature was varied from 200 °C to 300 °C. A post-annealing process has also been tested in vacuum with the temperatures of 300 °C, 400 °C, and 500 °C for 60 min. The films sputtered at RT are set as

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the comparison group. The films thicknesses were controlled within 350–400 nm.

The optical reflectance and transmittance of the films were measured by an UV–vis-NIR spectrophotometer. The carrier concentration and the Hall mobility of the films were obtained at room temperature by the Van der Pauw method on Hall system NANOMETRICS HL5500PC with liquid metal (In–Ga eutectoid alloy) electrodes. X-ray diffraction (XRD) was carried out by DMAX 2500V (Rigaku) using Cu Ka lines (0.1541 nm). The chemical states and valence band of the films were examined by X-ray photoelectron spectroscopy (XPS, 250 XI) with a monochromatic Al Kα (1486.6 eV) radiation source. The carbon 1s line was calibrated as corresponding to 284.6 eV.

3. Results and discussion

The optical band gaps of SnO and SnO_2 are 2.7–3.2 eV [16] and 3.7 eV [17], respectively. In order to investigate the alteration of optical band gaps and the evolution of tin oxides while increasing the O_2 ratio, optical reflectance (R) and transmittance (T) spectra were measured. The absorption coefficient (α) can be obtained by the following formula [18]:

$$T = (1 - R)e^{-\alpha d}$$

where d is the film thickness. The optical band gap is obtained by Tauc's plots, by extrapolating the linear part of $(\alpha h\nu)^2$ vs $h\nu$ curve to zero, where ν is the photon frequency. Fig. 1. shows the influences of O_2 ratio on the optical band gaps of SnO_x films. The SnO_x films can be classified into three groups according to their optical band gaps, marked as group I, II, III, respectively. For group I, the optical band gaps are less than 2.6 eV, which are smaller than the optical band gaps of SnO. The reason for the band gap narrowing may relate to the presence of metallic Sn, which makes these films dark brown. And the band gaps in group I reduce with the decrease of the substrate temperature. For group II, the optical band gaps locate between 3.0–3.3 eV, which matches the experimental optical band gaps of SnO. The band gaps are not wide enough to transparentize the films in the whole visible range. Therefore, the films in group II are yellowish. The band gaps in group III become wider, rising to about 3.6–3.7 eV, which are close to the optical band gaps of SnO_2 and make the films colorless. The films in group III exhibit good transmittance of larger than 75% in the visible range with a film thickness about 350 nm.

Fig. 2. illustrates the resistivity of the deposited SnO_x films as functions of the O_2 ratio. All of the films in group III are n-type,

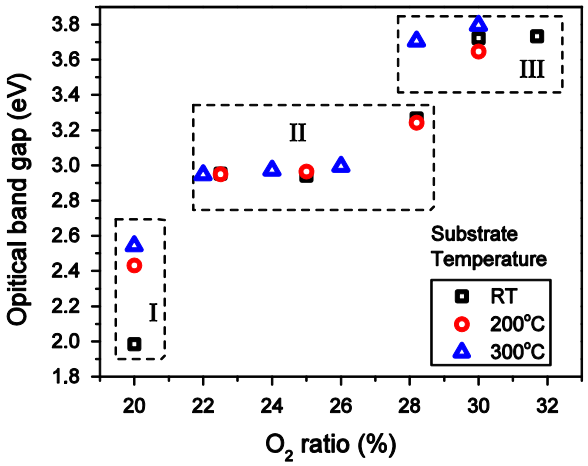

Fig. 1. Optical band gaps of sputtered SnO_x films as functions of the O_2 ratio.

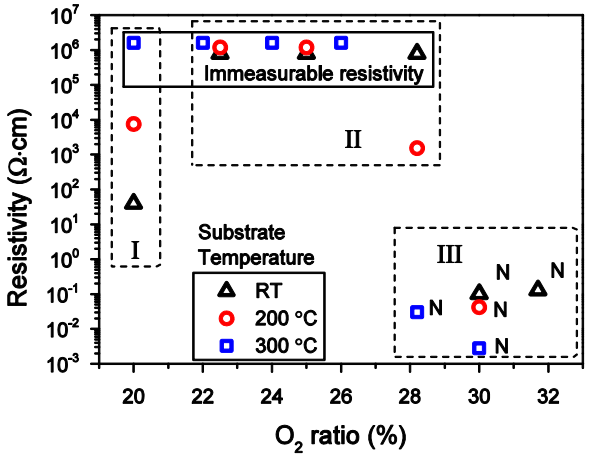

Fig. 2. Resistivity of sputtered SnO_x films as functions of O_2 ratio. The letter "N" around the data points stands for n-type conduction. The values in the "immeasurable resistivity" region are drawn schematically.

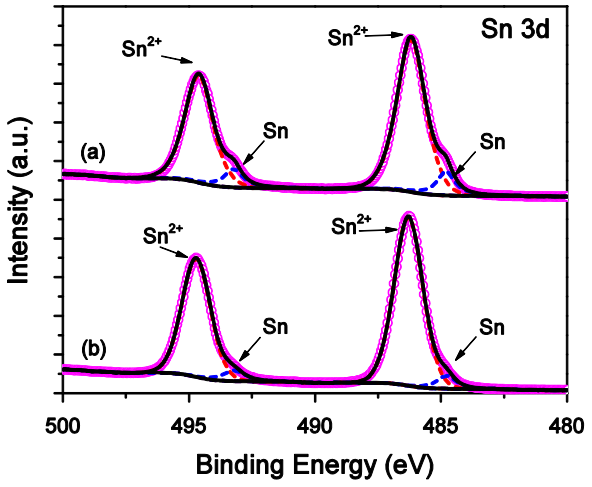

Fig. 3. Sn 3d core level scan of SnO_x films sputtered at different substrate temperatures with 20% O_2 ratio. (a) RT; (b) 300 °C.

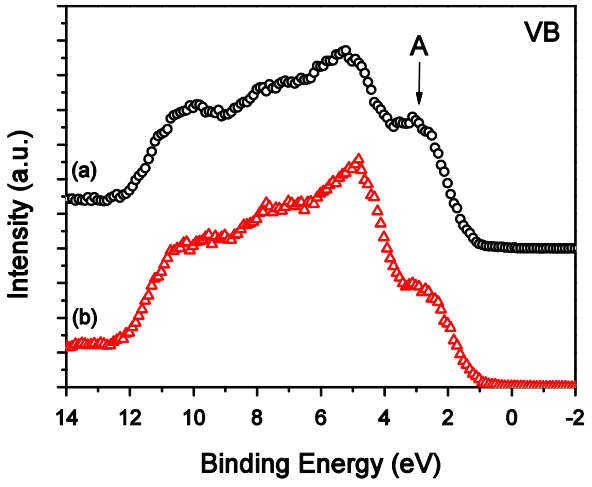

Fig. 4. The valence band scan of SnO_x films sputtered at different O_2 ratios with the substrate temperatures of 300 °C. (a) 26%, (b) 30%.

which implies that these films in group III may predominately consist of SnO_2 because SnO_2 is a nature n-type semiconductor. The optical band gaps illustrated in Fig. 1 also support this deduction. The electric resistivity of films in group III greatly