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Highly thermal stable transparent conducting SnO_2:Sb epitaxial films prepared on α-Al_2O_3 (0 0 0 1) by MOCVD

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ABSTRACT

Antimony-doped tin oxide (SnO_2:Sb) single crystalline films have been prepared on α-Al_2O_3 (0 0 0 1) substrates by metal organic chemical vapor deposition (MOCVD). The antimony doping was varied from 2% to 7% (atomic ratio). Post-deposition annealing of the SnO_2:Sb films was carried out at 700–1100 °C for 30 min in atmosphere ambient. The effect of annealing on the structural, electrical and optical properties of the films was investigated in detail. All the SnO_2:Sb films had good thermal stability under 900 °C, and the 5% Sb-doped SnO_2 film exhibited the best opto-electrical properties. Annealed above 900 °C, the 7% Sb-doped SnO_2 film still kept high thermal stability and showed good electrical and optical properties even at 1100 °C.

1. Introduction

Transparent conducting oxide (TCO) films have been studied for many years because of their importance in various fields such as opto-electronic devices and gas sensors. Among the available TCOs, SnO_2 thin films have been widely used as transparent electrodes in many fields such as solar cells, flat panel displays, and heat mirrors owing to its high transmission and conductivity [1–4]. In addition, SnO_2 films are more chemically stable than other TCOs such as zinc oxide (ZnO) and Sn-doped In_2O_3 (ITO) [5,6]. The resistivity of undoped SnO_2 films is dependent upon oxygen vacancies whose concentration is usually difficult to control. Therefore, the doping method is preferable in which a suitable dopant is added to SnO_2 to increase the carrier concentration. Antimony and fluorine are commonly used as dopants [7].

The SnO_2:Sb films have been prepared by various techniques, such as chemical vapor deposition [8], metal organic deposition [9], rf sputtering [10], sol–gel [11], and spray pyrolysis [12]. However, the electrical and optical properties of the SnO_2:Sb films are usually unstable under high temperature condition, which greatly limits the application of the films. Thus, thermal stability is a great concern in the fabrication and application of the films. Our earlier publication reported the fabrication and investigation of SnO_2:Sb single crystalline films prepared by MOCVD [13]. In this article, the structural, electrical and optical properties influenced by annealing for the obtained films are investigated in detail and SnO_2:Sb films with high thermal stability are reported.

2. Experimental procedure

The deposition of the films was carried out using an MOCVD system at 600 °C. Commercially available tetraethyltin {$Sn(C_2H_5)_4$} and trimethylantimony {$Sb(CH_3)_3$} were used as the organometallic (OM) sources. Detailed growth parameters of the SnO_2:Sb films are summarized in our previous study [13]. Post-deposition annealing of the SnO_2:Sb films was carried out at 700–1100 °C for 30 min in atmosphere ambient.

The structural properties were determined by a Philips X'Pert Pro MPD X-ray diffractometer (XRD) with Cu Kα radiation. A cross-sectional sample was made by gluing two pieces together with the thin films facing each other, followed by mechanical polishing and ion-milling to obtain a thin area suitable for transmission electron microscopy observation. High-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) were then performed on the sample by using a Technai F30 transmission electron microscope operated at 300 kV. The film thickness was measured using the Rutherford backscattering spectroscopy (RBS) technique. The sheet resistivities were

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determined with a conventional four-probe instrument. The Hall measurements were made with Van der Pauw technique. The optical transmittance measurements were performed with a Shimadzu TV-1900 spectrophotometer.

3. Results and discussion

Fig. 1a and b shows the low magnification cross-sectional transmission electron microscopy (XTEM) image and HRTEM image of the interface area between the SnO_2:Sb film and the Al_2O_3 substrate for the 2% Sb-doped sample, respectively. The SAED pattern is shown in the inset of Fig. 1b, which includes both the sapphire substrate and the SnO_2:Sb film. Fig. 1a shows a clean interface between the film and the substrate. From Fig. 1b, it can be seen that the as-prepared film is structurally uniform single crystalline, and the growth direction of SnO_2 film is [2 0 0]. For the substrate, the interplane spacing marked by the arrows is 0.436 nm, which is consistent with Al_2O_3 (0 0 0 3). For the SnO_2:Sb film, the interplane spacing is 0.237 nm, which is corresponding to SnO_2 (2 0 0) of rutile structure. The HRTEM analysis of the interface confirms that the 2% Sb-doped SnO_2 film is single crystalline with an epitaxial relationship of SnO_2 (1 0 0)||Al_2O_3 (0 0 0 1). The as-deposited SnO_2:Sb films with Sb-doping below 5% in our study have the similar structure and are single crystalline [13].

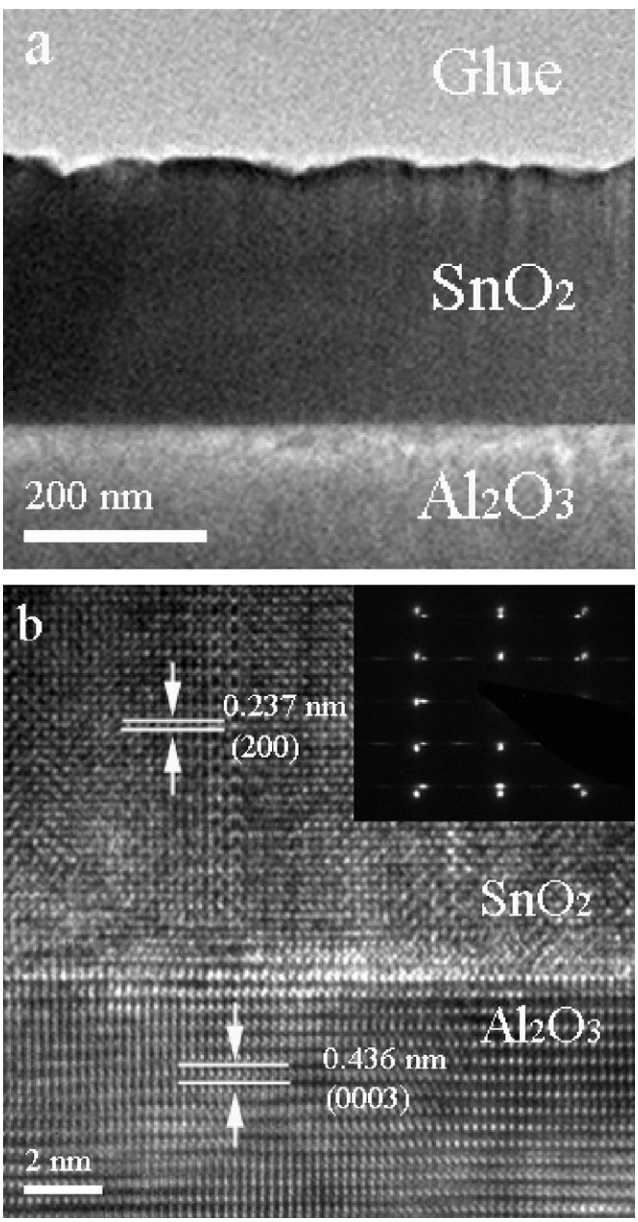

Fig. 1. (a) Low magnification XTEM image of the 2% Sb-doped sample. (b) HRTEM micrograph of the interface area between the SnO_2:Sb film and the Al_2O_3 substrate with corresponding SAED pattern in inset.

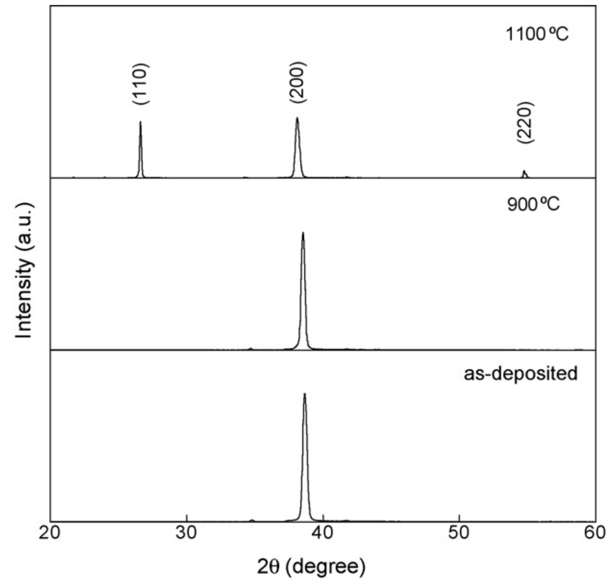

Fig. 2. XRD spectra of the 5% Sb-doped SnO_2 films before and after annealing at different temperatures.

Fig. 2 shows the XRD spectra of the 5% Sb-doped SnO_2 films before and after annealing at different temperatures. It can be seen that for the as-deposited and 900 °C annealed films, only a single strong diffraction peak corresponding to SnO_2 (2 0 0) reflection of rutile structure is observed, and no other phase is detected from the XRD patterns. After annealing at 900 °C, the location of peak (2 0 0) does not change obviously, but the full width at half maximum (FWHM) of peak (2 0 0) decreases slightly, which reveals an improvement in the crystalline quality. As annealing temperature increases further to 1100 °C, the (1 1 0) and (2 2 0) diffraction peaks of rutile structure SnO_2 appear and the location of peak (2 0 0) shifts towards low θ direction obviously, indicating an increase in the interplane spacing of SnO_2 (2 0 0) and a

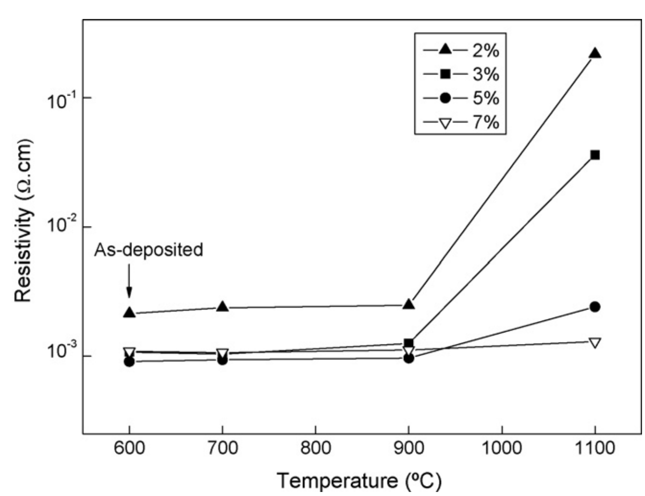

Fig. 3. Annealing temperature dependence of resistivity for the SnO_2:Sb films.