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Electrical, structural, photoluminescence and optical properties of p-type conducting, antimony-doped SnO_2 thin films

J. Ni, X. Zhao *, X. Zheng, J. Zhao, B. Liu

Key Laboratory of Silicate Materials Science and Engineering, Wuhan University of Technology, Ministry of Education, 122 Luoshi Road, Hongshan District, Wuhan, Hubei 430070, China

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Abstract

P-type transparent conducting antimony-doped tin oxide (ATO) films were successfully fabricated on quartz glass substrates by radio-frequency magnetron sputtering using a 20 mol.% Sb-doped SnO_2 ceramic target. The deposited films were annealed at different temperatures for different durations. Hall effect results indicated that 973 K was the optimum annealing temperature to get p-type ATO films with the highest hole concentration (5.83×10^{19} cm^{-3}). X-ray diffraction studies indicated that the preferred (1 0 1) orientation favored the formation of p-type conducting films. Photoluminescence spectra showed an intense UV luminescence peak near 362 nm resulting from the band-edge exciton transition observed for p-type ATO films. UV–visible transmission spectra showed that p-type ATO films had high transparence. In addition, p-type conductivity was also confirmed by the non-linear characteristics of a p-type ATO/n-type ATO structure; the diode structure has an optical transmission of ~60–85% in the visible light range.

Keywords: P-type SnO_2 thin films; Annealing; Sputtering; Semiconductor devices

1. Introduction

SnO_2 is a transparent wide-band-gap oxide semiconductor which is applied widely in many fields such as architectural windows, optoelectronic devices [1,2], solar cells [3], flat panel displays [4] and gas sensors [5], owing to its good optical and electrical properties and excellent chemical and thermal stability. It is well known that widely-used transparent conducting oxide (TCO) thin films such as ZnO, SnO_2, SnO_2:In are n-type because of the existence of intrinsic defects (oxygen vacancies and/or metal interstitials) [6], but research on p-type TCOs has only begun in recent years.

The majority of p-type TCOs have the delafossite structure with a general chemical formula of AMO_2, for example $CuGaO_2$ [7,8], $SrCu_2O_2$ [9], $CuAlO_{2+x}$ [10], $CuYO_2$:Ca [11] and $CuCr_{1-x}Mg_xO_2$ [12]. However, there are efforts to find an effective way to achieve p-type conduction in the generally n-type conducting oxides such as ZnO and SnO_2. This has opened up a new field in optoelectronics device technology, the so-called "transparent electronics", where a combination of the two types of TCO in the form of a p–n junction [13] could lead to a "functional" window, which transmits in the visible portion of the solar spectrum, yet generates electricity by absorption in the UV portion [14].

Recently, p-type doping of SnO_2 thin films was studied using elements with a lower valence cation as the acceptor impurity, which increases the hole concentration. For example, aluminium-doped SnO_2 thin films were reported by Ahmed et al. [14] and Mehdi et al. [15]. Mehdi et al. also reported the electrical, optical and structural properties of Li-doped SnO_2 thin films synthesized by the spray pyrolysis technique [16]. Very recently, Ji et al. [17] reported the synthesis of p-type indium-doped SnO_2 thin films by a sol–gel dip coating technique. Later, Ji et al. [18] also reported that p-type conducting indium-doped SnO_2 thin films were

* Corresponding author. Tel.: +86 2787652553.
E-mail address: opluse@whut.edu.cn (X. Zhao).

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deposited by spray pyrolysis. These results suggested that p-type SnO_2 thin films could be synthesized by a lower valence cation as acceptor impurity. However, the hole concentration of p-type SnO_2 films obtained using the above-mentioned methods was $\sim 10^{17}$–10^{18} cm^{-3}. Among various possible acceptor dopants, few papers reported the effective substitution of Sn by trivalent Sb for preparing p-type SnO_2 thin films and p–n homojunctions consisting of p-type SnO_2 thin films. Modulation of the band gap while keeping the lattice constants similar to each other is essential [19]. Because the ionic radius of Sb ions (0.90 Å for Sb^{3+} [20]) is similar to that of Sn^{4+}(0.83 Å), a wide range solubility of Sb in the Sn blend could be obtained in the films.

The most common preparation method for p-type SnO_2 thin films is the sol-gel technique. The results were not as satisfying as expected because of the poor film quality and limited film thickness. The RF magnetron sputtering technique is an effective technique adapted for production because of its high throughput, controllable thickness, as well as high uniformity and flexibility. Therefore, this paper studies the electrical, structural, photoluminescence (PL) and optical properties of p-type conducting, Sb-doped SnO_2 thin films deposited on quartz glass substrates by RF magnetron sputtering.

2. Experimental techniques

Bulk Sb-doped SnO_2 ceramic targets were prepared using Sb_2O_3 powder (99.9% purity) and SnO_2 powder (99.9% purity) as raw materials. The powder was pressed to form the pellets of mol mixture ratio for Sb_2O_3:$SnO_2 = 0.2$:0.8, which were sintered at $\sim$1523 K for 5 h and then cooled slowly to room temperature in an argon gas (99.999% purity) ambient. The 5.6-cm-diameter ceramic targets obtained were used for depositing the Sb-doped SnO_2 films by RF magnetron sputtering. The quartz glass substrates were cleaned in an ultrasonic bath with alcohol for 35 min.

The substrate temperature for sputtering was kept at 473 K. Before deposition, the target was pre-sputtered for 10 min to remove any contaminants on the target surface. The base pressure of the deposition system was 1×10^{-3} Pa. During sputtering, the pressure increased to 1 Pa as argon gas (99.999% purity) was introduced into the chamber; no oxygen gas was supplied. The sputtering power was 100 W. All the films were deposited for 30 min with a typical thickness of $\sim$800–850 nm, as observed from cross-sectional scanning electron microscopy (SEM). After deposition, the films were rapidly annealed at various temperatures ranging from 823 to 1073 K in air for $\sim$2–4 h.

Room temperature Hall-effect measurements were conducted using a HL5500PC system (Accent Optical, UK). X-ray diffraction (XRD) patterns were obtained using an X'pert PRO X-ray diffractometer with Cu K_α radiation (40 kV, 40 mA). The transmittance of the films in the wavelength range 250–800 nm was measured using a UV–Vis spectrophotometer (UV1601, SHIMADZU). The surface morphology was observed with an S-4800 field-emission scanning electron microscope manufactured by the Hitachi Company. The PL spectrum was measured using a RF5301 system (Shimadzu). A Xe lamp with 320 nm emission wavelength was used as the excitation light source. The I–V characteristics were measured using a semiconductor characteristic analyzer system (Keithley 4200-SCS).

3. Results and discussion

3.1. Electrical properties

The Hall measurement results at room temperature are shown in Table 1. It is seen that the annealing temperature plays an important role in the electrical properties of the ATO films. As seen in Table 1, the conducting type and carrier concentration of the ATO films depend on the annealing temperature with a critical point of $\sim$873 K in the temperature range 823–973 K. For the ATO films annealed at a temperature <873 K, the ATO films are n-type, and the electron concentration decreases with an increase in temperature; whereas at 873 K $< T \leq$ 973 K, the ATO films show p-type conductivity. The hole concentration increases with increasing temperature in the same range. However, for $T \geq$ 1023 K, the hole concentration decreases with increasing temperature; when the annealing temperature is 1073 K, the ATO films change to n-type again.

The above results regarding the change of carrier type and carrier concentration may be explained as follows:

Table 1
Results of the Hall effect measurements of SnO_2:Sb films annealed at different temperatures

Temperature (K)	Concentration (cm^{-3})	Mobility ($cm^2\ V^{-1}\ s^{-1}$)	Resistivity (Ω cm)	Type
No annealing	−2.59e+20	2.44e−1	9.90e−2	n
823 K for 4 h	−2.32e+20	9.39	2.87e−3	n
873 K for 4 h	1.50e+18	1.47e+1	2.83e−1	p/n
	−1.62e+18	1.36 e+1		
923 K for 4 h	3.05e+18	7.23	2.50e−1	p
973 K for 2 h	2.19e+16	3.13 e+1	9.12	p
973 K for 4 h	5.83e+19	6.47e−1	1.66e−1	p
1023 K for 4 h	1.54 e+16	6.28	1.52e+1	p
1073 K for 4 h	−4.58e+19	9.15	1.49e+1	n