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High figure of merit transparent conducting Sb-doped SnO_2 thin films prepared via ultrasonic spray pyrolysis

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ABSTRACT

Doped tin oxide has been studied extensively because of its potential as a replacement for indium tin oxide in transparent conducting oxide layers. Antimony-doped tin oxide (ATO) is one of the most promising materials in this regard, due to its superior transparency in the visible region and broad scope for electrical property improvements. In this paper, we report the fabrication of highly conductive transparent ATO thin films using a simple, low-cost ultrasonic spray pyrolysis method. A film with a resistivity of 5.8×10^{-5} Ω cm, transmittance of 88% at 550 nm, and figure of merit as high as 47.22×10^{-2} $(\Omega/cm^2)^{-1}$ was produced by tuning the deposition time. The ATO films produced in this experiment may be used as transparent conducting films with performance comparable to that of indium tin oxide.

1. Introduction

Transparent conducting oxides (TCOs) are important components of modern optoelectronic devices such as solar cells [1], sensors [2], flat panel displays [3–5], and light-emitting diodes (LEDs) [3]. The basic specifications for TCOs intended for use in this field include a resistivity no higher than 10^{-3} Ω cm and visible light transmittance of at least 80% [4]. Of the various transparent oxide layers available, SnO_2 films tend to attract significant attention because they are chemically, thermally, and mechanically stable [5–12]. Indium-doped SnO_2 (ITO) holds the largest share of the industrial market due to its high transmittance (>85%) and low resistivity in the order of 10^{-5} Ω cm [6]. However, indium is a rare-earth material with limited availability, and is thus expensive. Antimony-doped tin oxide (ATO) is considered a potential candidate for TCO applications because it offers relatively high transparency in the visible region and electrical conductivity comparable to that of ITO. Several ATO thin film growth techniques have been demonstrated, including pulsed laser deposition (PLD) [13], chemical vapor deposition (CVD) [14,15], sputtering [16–19], and wet-chemical methods such as sol-gel synthesis [20,21], electrospraying [22], and spray pyrolysis [6,23–27]. Of these, the last offers several advantages including simplicity, a controlled approach to doping, reproducibility, a high growth rate, the ability to uniformly cover a large area, and low cost, all of which are desirable for mass production [28]. Furthermore, ultrasonic-assisted spray pyrolysis offers additional high-quality thin film preparation advantages. For example, ATO films can be prepared on Ti substrates at growth temperatures as high as 600 °C using a precursor solution of $SnCl_4$, $5H_2O$, and $SbCl_3$, dissolved in hydrochloric acid. These films exhibit excellent electrical properties that can be varied by controlling the Sb doping concentration, with the optimum doping level being 3%. Their optimized electrical resistivities can be as low as 8.2×10^{-4} Ω cm [23]. Gupta et al. has demonstrated the fabrication of an ATO thin film at a lower growth temperature of 425 °C. A thin film with a conductivity and thickness as high as 1.512×10^{-3} Ω cm and 1–2 μm, respectively, was prepared on a glass substrate using 1.5 wt% Sb [6]. However, its optical

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transmittance was low, particularly at the visible light wavelength of 550 nm (35%). Rita et al. prepared an ATO thin film at an even lower temperature of 400 °C [24]. An ATO film with a resistivity as low as 1.121×10^{-3} Ω cm and transmittance of 80% at 550 nm was achieved using the precursor $SnCl_4$, $5H_2O$, and $SbCl_3$, dissolved in methanol (5 mol% Sb). The Babar group produced films with better electrical properties [25] by using a similar precursor with doubly distillated water as the solvent. They successfully fabricated ATO thin films with resistivities in the order of 10^{-4} Ω cm and transmittances of 75% in the visible region. Meanwhile, Gurakar et al. fabricated films with transmittances of over 80% [26] using tin chloride dehydrate [$SnCl_2 \cdot 2H_2O$) and $SbCl_3$ dissolved in hydrochloric acid and ethanol. The best-performing ATO film was reported recently by Yadav et al. [29,30]. By using 1 M $SnCl_4$:$5H_2O$ and 1.5 wt% $SbCl_3$ in isopropanol at a growth temperature of 550 °C, a film with a resistivity as low as 3.76×10^{-4} Ω cm and transmittance of 86% at 550 nm was synthesized on a glass substrate. However, despite the excellent films produced to date, a resistivity on the order of 10^{-5} Ω cm (comparable to ITO) has still to be achieved.

In this paper, we report the fabrication of ATO thin films with high conductivities and transparencies via a simple, ultrasonic-assisted spray pyrolysis technique. This method uses a 1 M mixed-ethanolic solution of $SnCl_2 \cdot 2H_2O$ and 2 wt% $SbCl_3$ as its precursor. By simply tuning the deposition time, a film composed of homogenous octahedron-shaped grains with low resistivity (~5.8×10^{-5} Ω cm) and high transparency (90% at 550 nm) was produced. The film exhibited an equivalent figure of merit as high as 47.22×10^{-2} $(\Omega/cm^2)^{-1}$. This ATO film exhibited much better properties than materials that have recently been reported [29,30]. Thus, our product may have potential applications as a TCO, as an alternative to ITO, and in solar cells and LEDs.

2. Experimental

As mentioned above, ATO thin films were prepared on glass substrates using ultrasonic-assisted spray pyrolysis. Our process was based on the best result obtained from a previous study [31]. The precursor solution used was 1 M $SnCl_2 \cdot 2H_2O$ (Merck), and antimony doping was kept constant at 2 wt% $SbCl_3$ (Merck). These were diluted in ethanol and stirred at 500 rpm for 1 h at a room temperature (25 °C) in closed vials. Ultrasonic-assisted spray pyrolysis was performed by using a commercial ultrasonic nebulizer (1.7 MHz) to grow the Sb-doped SnO_2 (ATO) thin films on glass substrates (2 cm × 2 cm x 0.1 cm). The substrates were heated on a hot plate at 450 °C during the process. The distance between the nozzle and the substrate surface was 3 cm. Deposition times of 10, 20, and 30 min were tested to determine the optimum conditions for high-quality ATO thin film growth.

The phase and crystallinity properties of the films were analyzed using an X-ray diffractometer (XRD, Shimadzu XRD-7000, CuKα radiation 1.54060 Å). XRD data acquisition conditions were as follows: 2θ range of 10–80°, scan speed of 2.00° min^{-1}, and steps of 0.01°. Surface morphologies and roughnesses were examined via scanning electron microscopy (SEM, JEOL JED-2300) and atomic force microscopy (AFM, NT-MDT), respectively. Film thicknesses were determined using cross-sectional SEM images. Optical absorbance and transmission properties were evaluated using a Thermo-Fisher Scientific GENESYS 10S UV–vis spectrometer. The PL spectrum was measured using a FLS920 fluorescence spectrometer (Edinburgh Instruments), with 300 nm light used for excitation. Electrical properties were measured in air at a room temperature (25 °C) using a Veeco Four Point Probe 5000 system and an Ecopia HMS-5300 Hall Effect measurement system.

3. Results and discussion

3.1. Thin film deposition and reaction mechanism

In spray pyrolysis, SnO_2 thin film formation start with the chemical reaction between stannous chloride ($SnCl_2 \cdot 2H_2O$) and $SbCl_3$, which produces a fully diluted stannic chloride solution.

$$3SnCl_2 \cdot 2H_2O + 2SbCl_3 \rightarrow 3SnCl_4 \cdot 2H_2O + 2Sb^{3+} \quad (1)$$

According to Babar [25] and Yadav [30], incomplete decomposition of $SnCl_4$ and oxidation of the film during pyrolytic decomposition results in oxygen vacancies with two positive charges. Chlorine ions and oxygen vacancies contribute to conductivity of undoped SnO_2. The anticipated reactions are [25,30],

$$2SnCl_4 + 4H_2O \rightarrow SnO_2 + SnO + 7HCl + \frac{1}{2}O_2 + \frac{1}{2}Cl_2 + \frac{1}{2}H_2 + e^- \quad (2)$$

or

$$2SnCl_4 + 4H_2O \rightarrow SnO_2 + SnO + 8HCl + \frac{1}{2}O_2 + 2e^- \quad (3)$$

The presence of Sb^{3+} can increase the number of oxygen vacancies via the following mechanism [25,30],

$$3Sb^{3+} \rightarrow 2Sb_{Sn} + V_O \quad (4)$$

While Sb^{5+} may increase the number of free electrons as follows [25,30],

$$2Sb^{5+} \rightarrow 2Sb_{Sn} + 2e^- \quad (5)$$

The presence of oxygen vacancies, ion charges, and free electrons results in high-conductivity ATO thin films [25,30].

3.2. X-ray diffraction

The X-ray diffraction patterns of ATO thin films prepared using three different deposition times are shown in Fig. 1. By comparing the patterns to JCPDS card 01-072-1147, it can be confirmed that all samples consist of single-phase ATO with a tetragonal rutile crystal structure. The six major peaks in the pattern correspond to the (110), (101), (200), (211), (310), and (301) diffraction planes. Increasing the deposition time from 10 to 20 min boosts all of the peak intensities, while ramping the time up to 30 min significantly enhances the intensity of the (211) peak. This indicates increases in the crystallinities of the ATO thin films [29,32]. The texture coefficients, lattice parameters, and crystallite sizes of the six major XRD peaks are shown in Table 1 for all samples.

The quantitative measurement of the preferred orientation is expressed by the texture coefficient TC of each (hkl) plane via the following relationship [17]:

$$TC(h_i k_i l_i) = \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \left[\frac{1}{n} \sum_{i=1}^{n} \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \right]^{-1} \quad (6)$$

where $I_0(h_i k_i l_i)$ is the standard intensity, $I(h_i k_i l_i)$ is the observed intensity of the $(h_i k_i l_i)$ plane, and n is the number of peaks. The films deposited for 10 min have the (110) plane as their preferred orientation, as demonstrated by its TC value. The films grown for 20 and 30 min display similar TC values (TC = 1) for all peaks, and thus exhibit no predominant orientation.

The calculated lattice parameters of the ATO films