The influence of Sb doping on the structural, optical and electrical properties of tin oxide thin film

M N Yusnidar¹, V Fauzia¹, D Handoko¹ and L Hanum²

¹Department of Physics, Universitas Indonesia, Depok, Indonesia
²Research Center for Metallurgy and Material LIPI, Serpong, Indonesia

E-mail: vivi@sci.ui.ac.id

Abstract. Antimony-doped Tin Oxide (Sb:SnO₂), shortened as ATO, has become more popular due to their great technological importance. ATO was considered as important transparent conducting material for optoelectronic devices and sensors application because of its unique and special characteristic such as high transparency in visible region, and high electrons concentration and mobility. In this study, the Sb:SnO₂ thin film have been fabricated with low cost and simple ultrasonic spray pyrolysis method. SnO₂ thin film was deposited with three different Sb concentrations namely 1, 2, and 3 wt%. The structural, morphological, optical and electrical properties of this film have been analyzed by using X-ray diffraction, scanning electron microscopy, UV-VIS and four point probe instruments. Based on the optical and electrical properties characterization, the best concentration of Sb doping was 2wt% because its transmittance was above 80% at all wavelength range measured, and the electrical resistivity was quite low, at 0.663 x 10⁻³ Ω cm.

1. Introduction

Transparent Conducting Oxide (TCO) film is an important part of technologies which requires both, large area of high electrical conductivity and optical transmittance in the visible region [1]. Antimony-doped Tin Oxide (Sb:SnO₂), shortened as ATO, is the promising TCO material due to non toxic antimony characteristic and it is cheaper than some common used doping materials, such as indium and fluorine [2]. The transparent conducting Sb:SnO₂ film have huge potential application in solar cells, light emitting diodes, flat panel display and biochemical sensors devices [3, 4]. An important key to adjust both optical transparency and electrical conductivity in the oxides is by controlling band gap energy and improving the free charge carriers. Hence, the electrical conductivity of TCO should be improved by increasing the number of free charge carries through intrinsic and extrinsic defects, such as oxygen vacancies and extrinsic dopants, typically higher-valence metal cautions [5].

ATO thin film could be deposited using various methods such as pulse laser deposition, sputtering, chemical vapor deposition, sol-gel, hydrothermal, and spray pyrolysis [2]. Spray pyrolysis is one promising technique to produce a conductive and transparent thin film in a cost-effective way because it could be operated in low temperature without high vacuum instrument [6].

In this paper, the Sb:SnO₂ thin film were deposited using ultrasonic spray pyrolysis method with metal salts SnCl₂·2H₂O, SbCl₃ as the precursor and ethanol as the solvent. The Sb:SnO₂ film were kept at temperature of 450°C with three different Sb doping concentrations. Based on Bendjedidi [7], the film which was deposited below 450°C were amorphous, whereas for the higher temperatures the
film crystalinity were increased hence the transmittance and electrical conductivity would be enhanced. In this paper, we would report the effect of antimony doping on the SnO\textsubscript{2} thin film properties such as morphology, crystal structure, optical and electrical properties.

2. Experimental
The precursor solutions containing 1M chloride dehydrate (SnCl\textsubscript{2}·2H\textsubscript{2}O) in ethanol and three different antimony chloride (SbCl\textsubscript{3}) concentrations (1, 2, 3 wt %) were stirred for an hour at room temperature. The deposition of Sb:SnO\textsubscript{2} thin film was carried out using ultrasonic spray pyrolysis. The precursor solutions were placed into a container in the commercial ultrasonic nebulizer (1.7 MHz) and sprayed for 10 minutes onto the glass substrate which were heated on a hotplate at a temperature of 450°C.

The structural properties Sb:SnO\textsubscript{2} thin film were observed using a powder X-ray diffractometer XRD-7000 with Cu-K\textalpha radiation in the angle range of 10°-80°. The morphology of the film was observed by scanning electron microscope (SEM) JEOL JED-2300. An optical spectrum of transmission, absorption, and reflectance at a wavelength range between 300 - 900 nm were monitored using GENESYS 10S UV-VIS Spectrometer and Hitachi UV-VIS Spectrometer U-3900H. The electrical properties were studied by using a Four Point Probe (FPP) 5000.

3. Result and discussion
3.1. Structural analysis
The X-ray diffraction patterns of Sb:SnO\textsubscript{2} thin film which were deposited at various Sb doping concentrations is shown in figure 1. All samples have five diffraction peaks at 26.61°, 33.92°, 37.99°, 51.84°, 61.95° and 66.05° corresponding to the (110), (101), (200), (211), (310) and (301) planes of tetragonal rutile crystal structure of the SnO\textsubscript{2} phase. According to this observation, other phases, such as SnO, Sb\textsubscript{2}O\textsubscript{3} and Sn\textsubscript{2}O\textsubscript{3}, did not exist in the deposited thin film. It indicated that the O atoms were replaced by Sb atoms in the Sb:SnO\textsubscript{2} thin film. For all samples, the intensity of (200) plane is more dominant than the intensity of other crystal planes, except for 1% Sb:SnO\textsubscript{2} sample. This low intensity is more likely appears as the result of a very thin layer was formed. Moreover, 1% and 2% Sb:SnO\textsubscript{2} samples show the amorphous phase at the 2\theta range of 20-35°. This characteristic was also shown in the SnO\textsubscript{2} thin film deposited by RF magnetron sputtering with post annealing treatment [2] and chemical spray pyrolysis [8]. The reason for the coexistence of amorphous phase in Sb:SnO\textsubscript{2} thin film still remains unclear.

![Figure 1. XRD patterns of Sb:SnO\textsubscript{2} thin film with three different Sb doping concentrations](image)
All samples show the same trend for growing along the (200) direction. The full width at half maximum (FWHM) of (200) peak are 0.7454°, 0.3461°, and 0.4169° for the SnO₂ film with Sb doping concentrations of 1, 2, and 3 wt %, respectively. The increasing FWHM value means the decreasing of crystallite size and vice versa. The crystallite size of the SnO₂ film with Sb doping concentrations of 1, 2, and 3 wt%, is 9.8 nm, 15.0 nm and 10.1 nm, respectively. Based on this data, there is no linear relationship between the Sb concentrations with the crystallite size.

3.2. Morphological properties

Figure 2 shows the SEM images of Sb:SnO₂ thin film deposited on glass substrate at various Sb doping concentrations. It was seen that the surface morphology of the film is strongly dependent on the doping concentration. The film appeared to have uniform distribution without cracks. Except for 1%Sb:SnO₂ thin film, the layers were more likely made up of octahedron-shape grains. The average of grain size increased by enhanced the Sb concentration. This output was similar to the result reported by Yadav et al. [5] who also found that the average grain size of Sb-doped SnO₂ thin film was larger than the pure SnO₂ thin film. Figure 3 shows the cross-sectional view of the thin film, where all thickness of the ATO thin film was in the order of 400 nm.

![Figure 2](image1)

**Figure 2.** SEM images of the SnO₂ thin film with Sb concentration of (a) 1, (b) 2, (c) 3 wt.%

![Figure 3](image2)

**Figure 3.** Cross sectional view of the SnO₂ thin film with Sb concentration of (a) 1, (b) 2, (c) 3 wt. %
3.3. Optical properties

Figure 4 shows the transmittance spectra of Sb:SnO$_2$ thin film with various Sb doping concentrations. According to the spectra, the addition of 1 and 2% Sb has increased the transmittance up to 80% at a wavelength range between 350 to 900 nm. This result meets the minimum transparency requirement for Transparent Conducting Oxide (TCO). The addition of 3% Sb has reduced the transmittance, down to 60%, because it could increase the rate of crystal defects. The huge defect might increase the light scattering, hence the transmittance would be reduced and the thin film became darker [9]. In contrast to the transmittance spectra result, the absorption spectra as seen in figure 4(b) shows that by increasing of Sb concentrations, the absorption was also enhanced at all wavelengths region.

![Figure 4](image1)

**Figure 4.** (a) Transmittance and (b) absorbance spectra of Sb:SnO$_2$ thin film with three different Sb doping concentrations

![Figure 5](image2)

**Figure 5.** (a) Reflectance spectra and (b) tauc plot of Sb:SnO$_2$ thin film with three different Sb doping concentrations
The optical band gap of the Sb:SnO\(_2\) thin film was determined using optical reflectance spectra and Tauc plot as shown in figure 5. The direct band gap for the Sb:SnO\(_2\) thin film with Sb concentrations of 1, 2 and 3 wt.% are 3.79 ±0.0537, 3.58 ± 0.0951 and 3.56 ± 0.2040 eV respectively. The direct band gap has decreased by increasing the Sb concentrations. Yadav et al. reported that the band gap energy increased from 3.76 eV to 3.80 eV for the Sb:SnO\(_2\) thin film 1 wt.% to 2 wt.% and then decreased to 3.72 eV for 3 wt.% [6]. The reduction of the band gap energy in this experiment is similar to those reported by Gurakar et al [10].

3.4. Electrical properties
The electrical resistivity values are tabulated in table 1. It shows that the increase of Sb concentrations could significantly reduce the resistivity, because Sb has been well known as an effective electrons donor, so that it might decrease the electrical resistivity of the thin film [5].

| Sb doping concentrations | Resistivity \((10^{-3} \Omega \text{ cm})\) |
|-------------------------|--------------------------|
| 1%                      | 165                      |
| 2%                      | 0.663                    |
| 3%                      | 0.1834                   |

Based on the optical characterization, the SnO\(_2\) thin film with Sb 1 and 2 wt.% appear to have higher transparency than those with Sb 3wt.%. However, the SnO2 thin film with Sb 1 wt.% comes out to have very high electrical resistivity. Therefore, it could be concluded that the optimum Sb doping concentration is 2 wt % because the transmittance is above 80% at wavelength range measured and the electrical resistivity as low as 0.663 x 10\(^{-3}\) \(\Omega\) cm. The results is better than the result, which was recently reported by Yadav et al who have successfully obtained the ATO thin film with an electrical resistivity as low as 0.704461 x 10\(^{-3}\) \(\Omega\) cm and the transmittance below 80% [5].

4. Conclusions
The antimony doped tin oxide thin film with three different Sb concentrations (1, 2 and 3 wt %) were synthesized by using ultrasonic spray pyrolysis method. Afterwards, the characterization and analysis were conducted to study the effect of Sb doping concentrations on the structural, optical and electrical properties. XRD pattern confirmed that the thin film was polycrystalline with tetragonal crystal structure. All samples show a preferential growth along the (200) crystal plane, while there is no linear relationship between Sb concentrations with the crystallite size. The SEM images showed that the film was made of continuous, uniform octahedron-shape grains without cracks. By increasing of Sb concentration, the grain size was increased; the transparency, direct band gap and the resistivity were decreased. Based on the optical and electrical properties characterization, the optimum Sb doping concentration should be used is 2 wt % because the transmittance is above 80% at all wavelength range measured and the electrical resistivity as low as 0.663 x 10\(^{-3}\) \(\Omega\) cm.

Acknowledgements
This work was supported by Hibah Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa (PITTA) 2016 Universitas Indonesia. The authors also would like to thank Prof. Dr. Muhamad Mat Saleh and Assoc. Prof. Dr. Akrajas Ali Umar From Organic and Printed Electronic Laboratory (OPEL) IMEN Universiti Kebangsaan Malaysia for this beneficial research collaboration.
References
[1] Ravichandran K and Philominathan P 2008 Mater. Lett. 62(17) 2980
[2] Zheng H, Li L, Sun Z, Yu S and Luo W 2016 Appl. Surf. Sci. 362 230
[3] Sharma S, Volosin A M, Schmitt D and Seo D K 2013 Chem. Mater. 1 699
[4] Yang W, Yu S, Zhang Y and Zhang W 2013 Thin Solid Films 542 285
[5] Yadav A A, Pawar S C, Patil D H and Ghogare M D 2015 J. Alloys Compd. 652 145
[6] Babar A R, Shinde S S, Moholkar A V, Bhosale C H, Kim J H and Rajpure K Y 2011 J. Semicond. 32(5) 1
[7] Bendjedid H, Attaf A, Saidi H, Aida M S, Semmari S and Bouhdjar A 2015 J. Semicond. 36(12) 2
[8] Orimi L R and Maghouli M 2016 Optik 127(1) 263
[9] Babar A R and Rajpure K Y 2015 J. Anal. Appl. Pyrolysis 112 214
[10] Gurakar S, Serin T and Serin N 2015 Appl. Surf. Sci. 352 16