Journal of Sensor Science and Technology
Vol. 31, No. 6 (2022) pp. 371-375
http://dx.doi.org/10.46670/JSST.2022.31.6.371
pISSN 1225-5475/eISSN 2093-7563

Effects of Substrate Temperature on Properties of Sb-doped SnO_2 Thin Film

Do Kyung Lee[1] and Young-Soo Sohn[2,+]

Abstract

Antimony-doped tin oxide (ATO) thin films, one type of transparent conductive oxide (TCO) films, were prepared on a SiO_2-coated glass substrate with different substrate temperatures by a radio-frequency magnetron sputtering system. Structural, optical, and electrical characteristics of the deposited ATO films were analyzed using X-ray diffraction, scanning electron microscopy, alpha-step, ultraviolet-visible spectrometer, and Hall effect measurement. The substrate temperature during deposition did not affect the basic crystal structure of the films but changed the grain size and film thickness. The optical transmittance of the ATO films deposited at different substrate temperatures was over 70%. The lowest sheet resistance and resistivity were 8.43×10^2 Ω/sq, and 0.3991×10^{-2} Ω·cm, respectively, and the highest carrier concentration and mobility were 2.36×10^{21} cm^{-3} and 6.627×10^{-2} cm^{2}V^{-1}s^{-1}, respectively, at a substrate temperature of 400 °C.

Keywords: Transparent conductive oxide, Sb, SnO_2, Substrate temperature, RF magnetron sputtering

1. INTRODUCTION

Transparent conductive oxide (TCO) films having exceptional optoelectrical properties, such as high transparency and electrical conductivity, are widely applied in devices such as flat panel displays, solar cells, sensors, and optoelectronic devices. [1–6] Indium tin oxide (ITO) is one of the most widely used materials for TCO films owing to its high transparency in the visible wavelength range, and low electrical resistivity. However, indium (In) is a relatively rare material, and ITO is brittle. [1]

Another promising candidate for a TCO material is tin oxide (SnO_2) because of its wide bandgap and good chemical and mechanical stability. [1] SnO_2 is known to be a wide bandgap (~3.6 eV) n-type semiconductor material with high transmittance in the visible wavelength range (380–780 nm), low transmittance in the near-infrared wavelength range (780–2500 nm), and good adhesion to glass. [3, 6–8] To meet the practical requirement of TCO films, transition metal ions can be doped into SnO_2 films to modify the bandgap of SnO_2. [3, 7] Among various dopants, In, F, and Sb are attractive because they improve electrical conductivity. As In is expensive, films doped with the relatively cheaper elements like F and Sb are of interest, and they show excellent chemical and thermal stability. [3, 6, 7] Door and window glasses with these films can save building energy owing to the above properties. [6] A blue-colored coating can be produced by doping Sb into SnO_2 films. [3]

Sb-doped SnO_2 (ATO) can be prepared by various deposition methods, including sputtering [9-11], spray pyrolysis [12], and sol-gel [7, 13]. Among the deposition techniques, the sputtering method has been widely used for fabricating TCO thin films because of its advantages of high growth rate, low cost, easy control, high growth efficiency for a good quality film, and suitability for large area deposition. [14] In addition, the deposition of very thin ATO films with under 100 nm thickness is important from the viewpoint of microelectronic application. Accordingly, studies on this topic will be of benefit in helping the design and fabrication of miniaturized devices.

In this work, ATO thin films were prepared by an RF (radio frequency) magnetron sputtering system. The effect of substrate temperature on the properties of ATO films was investigated.

2. EXPERIMENTAL

ATO films were prepared on a SiO_2/glass substrates by an RF -magnetron sputtering system. A ceramic target of 95% SnO_2 and

[1]School of Advanced Materials Science and Chemical Engineering, Daegu Catholic University, 13-13 Hayang-ro, Gyeong-san, Gyeongsangbuk-do 38430, Republic of Korea
[2]Department of Biomedical Engineering, Daegu Catholic University, 13-13 Hayang-ro, Gyeong-san, Gyeongsangbuk-do 38430, Republic of Korea
[+]Corresponding author: sohnys@cu.ac.kr
(Received: Oct. 29, 2022, Revised: Nov. 22, 2022, Accepted: Nov. 24, 2022)

Table 1. Sputtering conditions for ATO film deposition.

Sputter parameters	
T-S distance	100 mm
RF power	30 W
Base pressure	1.5×10^{-6} Torr
Ar flow rate	20 sccm
Sputtering time	10 min.
Alloy target	SnO_2 : Sb_2O_3 (95:5)
Substrate	SiO_2/glass
Substrate temperature	200, 300, 400, 500 °C

5% Sb_2O_3 with a diameter of 3 inches was used. After establishing a vacuum chamber of 1.5×10^{-6} Torr in the RF magnetron sputtering system, Ar gas was introduced at a flow rate of 20 sccm. The working power, sputtering time, and target-to-substrate distance (T-S distance) were 30 W, 10 min, and 100 mm, respectively. The substrate temperature was varied from 200 to 500 °C. The sputtering conditions for ATO film deposition are summarized in Table 1.

The crystallinity of the ATO films was determined with an X-ray diffractometer (XRD, Rigaku, D/Max-IC), and the film thickness was measured using an alpha-step (α-step, KLA, Tencor). The surface morphology of the deposited films was observed by the scanning electron microscope (SEM, Hitachi S-4200). Transmittance spectra were produced using an ultraviolet-visible spectrometer (Shimadzu, UV-1601PC). The electrical characteristics of the ATO films, such as sheet resistance and carrier concentration, were measured by Hall effect measurement (Ecopia, HMS-3000).

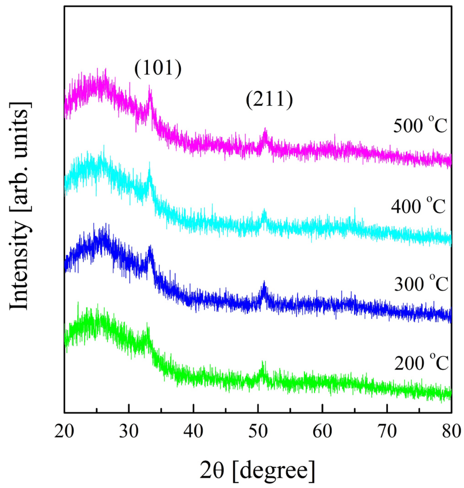

Fig. 1. XRD patterns of ATO films deposited on SiO_2/glass substrates at different substrate temperatures.

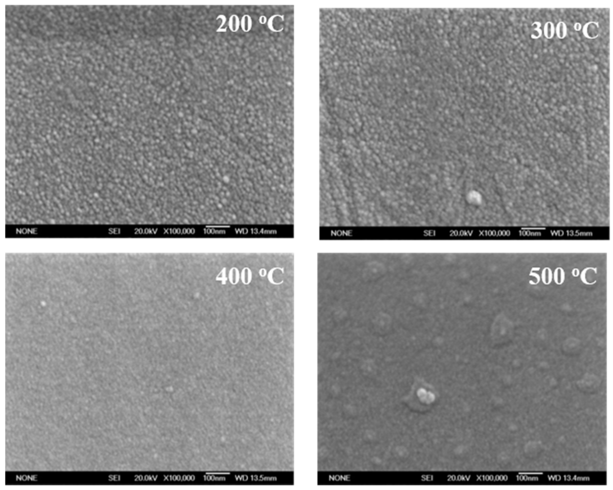

Fig. 2. SEM images of ATO films deposited on glass SiO_2 substrates at different substrate temperatures.

3. RESULTS AND DISCUSSION

3.1 Structural properties

Fig. 1 shows XRD patterns of ATO films deposited on SiO_2/glass substrates at different substrate temperatures. Three diffraction peaks at approximately 26.6°, 33.8°, and 51.7° are observed for the deposited ATO films. These peaks correspond to the (110), (101), and (211) planes, respectively, and they indicate the cassiterite tetragonal structure for SnO_2 (according to JCPDS card no 41-1445). [12] These peaks do not change significantly with the substrate temperature in the range of 200–500 °C; thus, crystallinity is not affected by temperature.

Fig. 2 shows the surface morphology of the ATO films. It can be observed that the grain size decreases, and the grain boundaries become less distinct as the substrate temperature increases from 200 °C to 400 °C. At 500 °C, there are a few large particles resulting from grain aggregation. This may be caused by an increase in the surface energy of the grains at this high substrate temperature. [6]

Fig. 3 shows the variation in ATO film thickness as a function of substrate temperature. The film thicknesses were 76.7, 71.3, 68.4, and 57.0 nm at substrate temperatures of 200 °C, 300 °C, 400 °C, and 500 °C, respectively. Thus, it can be concluded that the thickness of the deposited film decreases with increasing substrate temperature.

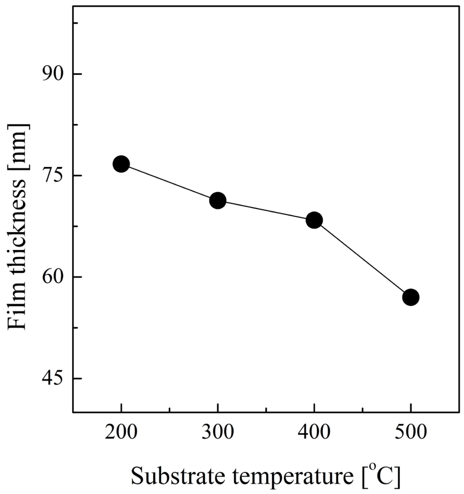

Fig. 3. Thickness of ATO films deposited on SiO_2/glass substrates at different substrate temperatures.

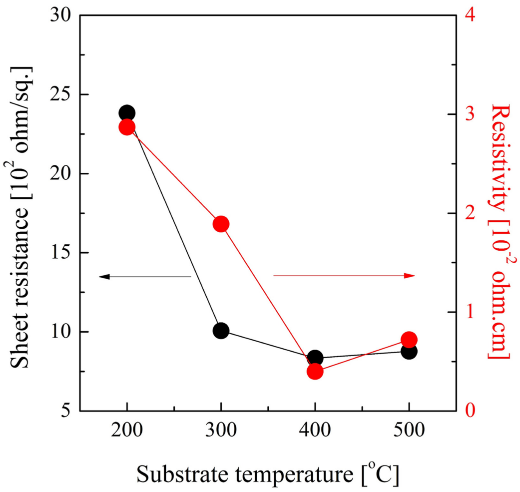

Fig. 5. Sheet resistance and resistivity of ATO films deposited on SiO_2/glass substrates at different substrate temperatures.

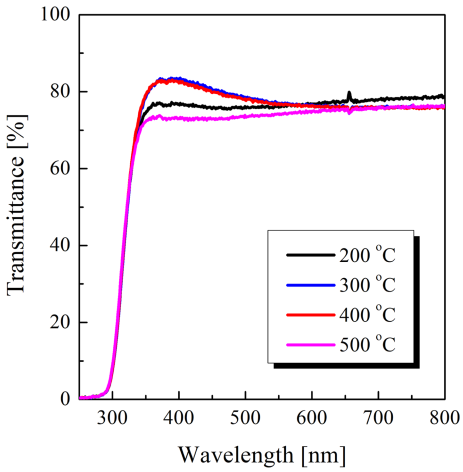

Fig. 4. Optical transmittance spectra of ATO films deposited on SiO_2/ glass substrates at different substrate temperatures.

3.2 Optical properties

Optical transmittance spectra of the ATO films in the range of 220–800 nm are shown in Fig. 4. In the wavelength range between 380 and 780 nm, the average transmittance of the ATO films deposited at the substrate temperature of 200 °C, 300 °C, 400 °C, and 500 °C is 76.9%, 77.9%, 77.5%, and 74.5%, respectively. For the films deposited at 300, and 400 °C, the transmittance is higher than the other two samples, and in particular, the transmittance in the blue region is higher than that in the other wavelength regions. Thus, these two films have an intense blue color, which has been frequently reported in literatures. [3, 15, 16]

3.3 Electrical properties

The effect of the substrate temperature on the electrical properties of the ATO films is illustrated in Figs. 5 and 6. Fig. 5 shows that as the substrate temperature increases from 200 to 400 °C, the sheet resistance and resistivity decrease significantly, while from 400 to 500 °C, the increase of both properties is quite small. In other words, the ATO film deposited with substrate temperature at 400 °C has the best conductivity. The sheet resistance and resistivity at this temperature were 8.43×10^2 Ω/sq and 0.3991×10^{-2} Ω·cm, respectively, which are lower than those of ATO films deposited by metal organic decomposition. [1]

For the application of the ATO films as transparent electrodes, the films must have low electrical resistance and high optical transparency. A useful tool for evaluating the performance of transparent electrodes is a calculation of the figure of merit (FOM). FOM is defined by

$$FOM = T^{10}/Rs,$$

where T is the average optical transmittance and Rs is the sheet resistance of the ATO films. [17] FOM value of the ATO films deposited at the substrate temperature of 200 °C, 300 °C, 400 °C, and 500 °C was 3.04×10^{-5} Ω^{-1}, 8.17×10^{-5} Ω^{-1}, 9.37×10^{-5} Ω^{-1}, and 6.01×10^{-5} Ω^{-1}, respectively. The highest FOM was at 400 °C, showing the optimal substrate temperature of the ATO films.

Fig. 6 shows the electron concentration and mobility of the ATO films deposited at different substrate temperatures between 200 °C and 500 °C. Since Sb has five valence electrons and is substituted for Sn, which has four valence electrons, the majority

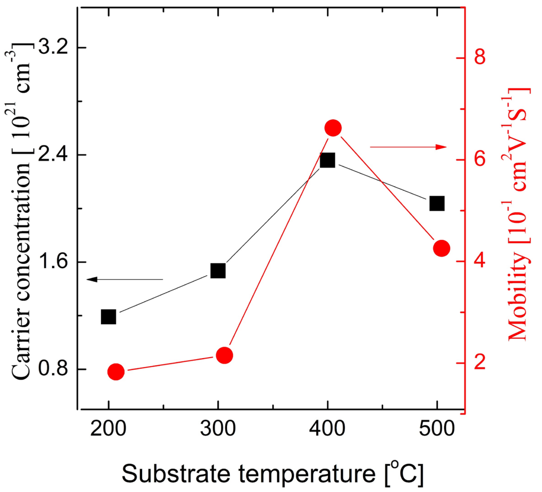

Fig. 6. Electron concentration and mobility of ATO films deposited on SiO_2/glass substrates at different substrate temperatures.

charge carrier is excess electrons, resulting in an n-type semiconductor. As the substrate temperature increases from 200 °C to 400 °C, the carrier concentration and mobility increase. This is likely because a more uniform surface reduces lattice scattering, which can improve mobility. At 500 °C however, as shown in Fig. 2(d), the aggregation of grains increases the level of defects in the deposited ATO film, resulting in a decrease in the mobility of the charge carrier. Thus, the optimized substrate temperature is 400 °C, and at this temperature, the charge carrier concentration and mobility were 2.36×10^{21} cm^{-3} and 6.627×10^{-2} $cm^2V^{-1}s^{-1}$, respectively.

4. CONCLUSIONS

ATO thin films were prepared on a SiO_2/glass substrate by an RF magnetron sputtering system. The effects of substrate temperature on the structural, optical, and electrical characteristics were investigated. The substrate temperature during deposition did not affect the basic crystal structure of the films, but the grain boundaries became less distinct as the substrate temperature increased to 400 °C. In addition, the thickness of the deposited ATO film decreased with increasing substrate temperature. The optical transmittance of the ATO films deposited at different substrate temperatures was over 70%. The lowest sheet resistance and resistivity were 8.43×10^2 Ω/sq, 0.3991×10^{-2} Ω·cm, respectively, and the highest carrier concentration and mobility were found to be 2.36×10^{21} cm^{-3} and 6.627×10^{-2} $cm^2V^{-1}s^{-1}$, respectively, at a substrate temperature of 400 °C. Considering the electrical and optical properties of the ATO films, the optimized substrate temperature is 400 °C.

ACKNOWLEDGMENT

This work was supported by research grants from Daegu Catholic University in 2022.

REFERENCES

[1] J. Sawahata and T. Kawasaki, “Structural and electrical properties of Sb-doped SnO2 thin films prepared by metal organic decomposition”, *Thin solid films*, Vol. 685, pp. 210-215, 2019.

[2] S. M. Rozati and S. A. M. Ziabari, “A review of various single layer, bilayer, multilayer TCO materials and their applications”, *Mater. Chem. Phys.*, Vol. 292, pp. 126789(1)-126789(22), 2022.

[3] S. D. Ponja, B. A. D. Williamson, S. Sathasivam, D. O. Scanlon, I. P. Parkin and C. J. Carmalt, “Enhanced electrical properties of antimony doped tin oxide thin films deposited via aerosol assisted chemical vapour deposition”, *J. Mater. Chem. C*, Vol. 6, pp. 7257-7266, 2018.

[4] L. Zhao, Y. Li, Y. Zhou, T. Wang, P. Sun, F. Liu, C. Wang, X. Yan, N. Chen, and G. Lu, “Mechanism of high- and low-valence doping on adsorbed oxygen of SnO2-based gas sensors and a strategy to combine the advantages of both dopants”, *Sens. Actuators B Chem.*, Vol. 371, pp. 132603(1)-132603(11), 2022.

[5] S. Huang, C. F. Guo, X. Zhang, W. Pan, X. Luo, C. Zhao,J.Gong, X. Li, Z. F. Ren and Hui Wu, “Buckled tin oxide nanobelt webs as highly stretchable and transparent photosensors”, *Small*, Vol. 11, pp. 5712-5718, 2015.

[6] M. Sun, J. Liu, and B. Dong, “Effects of Sb doping on the structure and properties of SnO_2 films”, *Curr. Appl. Phys.*, Vol. 20 pp. 462-469, 2020.

[7] Y. Bouznit and A. Henni, “Characterization of Sb doped SnO2 films prepared by spray technique and their application to photocurrent generation”, *Mater. Chem. Phys.*, Vol. 233, No. 1, pp. 242-248, 2019.

[8] M. Gao, H. Yang, M. Guo, X. Hu, H. Tian, Z. Liang, and P. Han, “Enhanced photoelectric performance of rutile SnO_2 by charge compensation effects modulated by Sb and N”, *J. Alloys Compd.*, Vol. 764, pp. 364-370, 2018.

[9] C. Guillén, and J. Herrero, “Intrinsic and extrinsic doping contributions in SnO_2 and SnO_2:Sb thin films prepared by reactive sputtering”, *J. Alloys Compd.*, Vol. 791, pp. 68-74, 2019.

[10] W. Yang, S. Yu, Y. Zhang, and W. Zhang, “Properties of Sb-doped SnO_2 transparent conductive thin films deposited by radio-frequency magnetron sputtering”, *Thin solid films*, Vol. 542, pp. 285-288, 2013.

[11] S. Jäger, B. Szyszka, J. Szczyrbowski, and G. Bräuer,

"Comparison of transparent conductive oxide thin films prepared by a.c. and d.c. reactive magnetron sputtering", *Surf. Coat. Technol.*, Vol. 98, pp. 1304-1314, 1998.

[12] D. Haouanoh, R.Z. Tala-Ighil, M. Toubane, F. Bensouici, and K. Mokeddem, "Effects of thermal treatment and layers' number on SnO2 thin films properties prepared by sol gel technique", *Mater. Res. Express*, Vol. 6, No. 8, pp. 086422(1)-086422(13), 2019.

[13] L.S. Chuah, S.S. Tneh, and Z. Hassan, "Synthesis of porous Ni-doped SnO2 thin film by using spray pyrolysis", *Compos. Interfaces* Vol. 18, pp. 371-376, 2011.

[14] S.-K. Wang, T.-C. Lin, S.-R. Jian, J.-Y. Juang, J. S.-C. Jang, and J.-Y. Tseng, "Effects of post-annealing on the structural and nanomechanical properties of Ga-doped ZnO thin films deposited on glass substrate by rf-magnetron sputtering", *Appl. Surf. Sci.*, Vol. 258, pp. 1261-1266, 2011.

[15] D.-W. Jung and D.-W. Park, "Synthesis of nano-sized antimony-doped tin oxide (ATO) particles using a DC arc plasma jet", *Appl. Surf. Sci.*, Vol. 255, pp. 5409-5413. 2009.

[16] E. Elangovan and K. Ramamurthi, "A study on low cost-high conducting fluorine and antimony-doped tin oxide thin films", *Appl. Surf. Sci.*, Vol. 249, pp. 183-196. 2005.

[17] G. Haacke, "New figure of merit for transparent conductors", *J. Appl. Phys.* Vol. 47, pp. 4086-4089, 1976.