THERMOELECTRIC PROPERTIES OF Sb-DOPED ZnO THIN FILM

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ABSTRACT

Sb-doped ZnO thin film was deposited on glass substrate by using a direct current (DC) magnetron sputtering system at ambient temperature. ZnO:Sb was premixed powder of of 1% and compacted into sintering at 1073 K for 20 h to be used sputtering target. The deposition times of 30, 45 and 60 min were used with deposition rate about 14 nm/min. Crystal structure, chemical composition, morphology, thickness determination, electrical resistivity and Seebeck coefficient at room temperature are investigated. It was found that, the crystal structure of as-deposited films of 30, 45 and 60 min were showed ZnO phases of (100), (200) and (101) planes. EDX results have been confirmed the Sb atomic mixed in ZnO structure successfully agreeing with XRD result. Films morphology showed the gains size in range 15-20 nm. Among the samples, the Sb-doped ZnO thin film deposited of 30 min showed the lowest electrical resistivity, and the highest power factor of 8.3×10^{-3} Ω m, and 3.09×10^{-6} W m^{-1} K^{-2}, respectively.

KEYWORDS: *DC magnetron sputtering; Thin film thermoelectric; Sb-doped ZnO thin film*

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INTRODUCTION

Zinc oxide (ZnO) is the wide direct band gap semiconductors (3.3 eV) [1–2, 3]. It has been recognized as promising technologies for clean energy production such as; solar cells [4] and thermoelectricity [5–7], etc. High performance of thermoelectric materials required the high dimensionless figure of merit (*ZT*) values as defined; $ZT = S^2T/\rho\kappa$, where *S*, ρ, κ and *T* are the Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively. Which S^2/ρ part is called thermoelectric power factor (*P*). Hence, good thermoelectric properties should be *S* is very high while ρ and κ are must very low. In addition, pure ZnO film based on n-type thermoelectric material had *S* as high as –200 μVK^{-1} [6] but has very high ρ (order of 10^4 Ω.m) [6]. It is leading to poor thermoelectric performance. However, based on metal doped ZnO can be reduced of ρ in to enhancing thermoelectric performance such as; Al metallic doped ZnO thin films exhibited electrical resistivity of seven order of magnitude as high as that of pure ZnO, but *S* is very low (–35 μVK^{-1}) [7]. Hence, ZnO thin films should be doped by semi-metallic to be few reduced of ρ and *S*.

In this work, the thermoelectric properties of ZnO thin film were enhanced by Sb doping through a DC magnetron sputtering process. The affected of deposition time onto microstructure and thermoelectric properties of Sb-doped ZnO thin film have been reported and discussed.

MATERIALS AND METHODS

Target preparation, the ZnO powder (99.99 % purity, QRëC, New Zealand) and Sb powder (99.99 % purity, Sigma-Aldrich, USA) were mixed in mortar within Zn:Sb; 0.99:0.01 ratio into pressuring in 60 mm of diameter and 3 mm of thick and then sintered at 1073 K for 20 hr. The $Zn_{0.99}Sb_{0.01}O$ target was loaded to target holder in vacuum chamber. While substrate preparation, Soda-lime glass plates of 2.5×2.5 cm^2 area was cleaned with acetone in ultrasonic washer for 10 min followed by drying in air, before loading at substrate holder in vacuum chamber. Thin film deposition, the Sb-doped ZnO thin film was deposited by an in-house-built dc magnetron sputtering system. Thin films deposition condition was base pressure 3.2 mT, working pressure 42 mT within Ar (99.99 % purity) gas, applied the dc power 30 W (GPR-100H05D, GWINSTEK, Taiwan) and varies deposition time 30, 45 and 60 min. Crystal structure of the films was investigated by X-ray diffraction (XRD-6100, Shimadzu). Elemental composition analysis carried out by energy dispersive spectroscopy (EDX) (JSM-5410, JEOL). Film morphology and thickness determination can be estimated by using the scanning electron microscope JSM-5410, JEOL). The film thickness of as-deposited thin films could be predicted the deposition rate. Electrical resistivity and Seebeck coefficient were measured by an in-house-built four-point probe and steady state methods at room temperature, respectively. A steady state method is Seebeck coefficient measurement based on the electromotive force (EMF) within an open circuit voltage and no current flow as determined by: $S = \Delta V / \Delta T$, where ΔV and ΔT were the electrical voltage and temperature differences, respectively [8].

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of Sb-doped ZnO thin films for deposition time of 30, 45 and 60 min indicating Hexagonal structure (P63mc space group) as confirmed by PDF#001-1136. This result demonstrated that the deposition time has been effected to crystalline growth up of Sb-doped ZnO thin films within (002) and (101) peaks for 30 min and (100), (022) and (101) peaks for 45 and 60 min. The XRD peak of (002) has been intensity changed with the deposition time to be corresponded the crystalline growth up. While the crystalline of thin film deposit 45 min has been tended minor difference. The XRD data of (002) peak could be calculated the crystal size (D) and lattice strain (ε) of Sb-doped ZnO thin films as shown in Table 1.

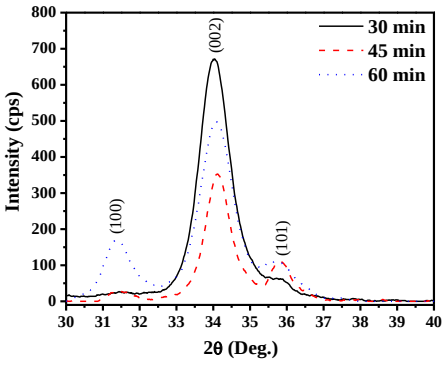

Fig. 1 XRD patterns of Sb-doped ZnO thin films deposit of 30, 45 and 60 min.

From Table 1, the crystal size of the thin film deposition time 30 min was minor increased for 17 nm to 20 nm of thin film deposition time 45 min and then decreased to 15 nm of thin film deposition time 45 min. This result caused the FWHM and lattice strain change from deposition time increasing. Also, this result was demonstrated that the Sb-doped ZnO thin films were Nano crystalline as confirmed by SEM images as shown in Fig. 2. The SEM images displayed the morphology and film thickness of Sb-doped ZnO thin films deposition time 60 min. The cross-section SEM images showed the film thickness of Sb-doped ZnO thin films deposition time 60 min approximately 833 nm to be obtained deposition rate of 14 nm/min. Fig.3 show the EDX result showed chemical composition of thin films. This result focused on Sb atomic composition investigation due to the minor percent of doping and then can be confirmed Sb-doped ZnO thin films successfully.

For thin film thermoelectric properties, the electrical properties were measured by four point probe method as shown in Table 2. The electrical resistivity of as-deposited thin films

Table 1 Crystal size and lattice stain of Sb-doped ZnO thin films

Deposition time (min)	Angle (002) peak (2Deg.)	FWHM (2Deg.)	Crystal size (nm)	Lattice strain (%)
30	34.04	0.97	17	0.69
45	34.12	0.82	20	0.58
60	34.08	1.08	15	0.77

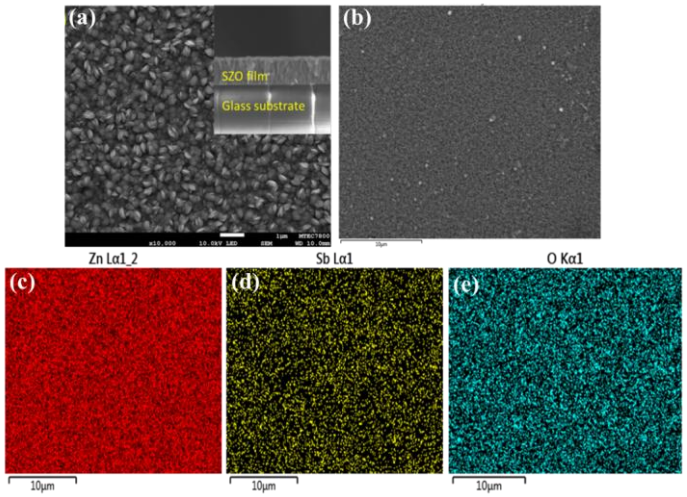

Fig. 2 (a) surface morphology and thickness, (b) surface morphology for EDX, (c), (d) and (e) surface mapping for EDX of Zn, Sb and O, respectively.

Table 2 Electrical properties of Sb-doped ZnO thin films

Deposition time (min)	$R_{ab,cd}$ (kΩ)	$R_{bc,da}$ (kΩ)	F	t (nm)	ρ (mΩ m)
30	5.6	3.37	0.9788	417	8.3
45	4.31	39.94	0.7120	625	44.6
60	101.48	310.16	0.9040	833	70.3

were calculated by using film thickness based on Van der Pauw method as followed;

$$\rho = \frac{\pi t}{\ln 2}\left(\frac{R_{ab,cd} + R_{bc,da}}{2}\right)F \quad (1)$$

which, $R_{ab,cd} = \frac{V_{cd}}{I_{ab}}$ and (2)

$$R_{bc,da} = \frac{V_{da}}{I_{bc}} \quad (3)$$

where t is film thickness, $R_{ab,cd}$ and $R_{bc,da}$ are resistance of film at *ab,cd* and *bc,da* point, and *F* is correction function as obtained from eq. (4).

$$\left|\frac{R_{ab,cd} - R_{bc,da}}{R_{ab,cd} + R_{bc,da}}\right| = \frac{F}{\ln 2}\arccos h\left[\exp\frac{\ln 2}{F} / F\right] \quad (4)$$

From Table 2, the electrical resistivity of the Sb-doped ZnO thin films were gradually increased from 8.3×10^{-3} Ωm to 70.3×10^{-3} Ωm with the increase in film deposition time due to film thickness and resistance increasing as related is eq. (1).

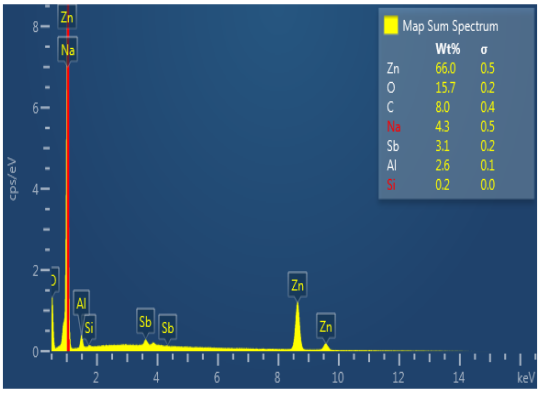

Fig.3 EDX spectra and atomic composition of the Sb-doped ZnO thin films.

Figure 4 shows Seebeck coefficient measurement with steady state method at room temperature. The Seebeck coefficient measurement result of Sb-doped ZnO thin films yielded the n-type thermoelectricity. The Seebeck coefficient measurement result of Sb-doped ZnO thin films has been increased from –160 μV K^{-1} to –263 μV K^{-1} with the deposition time increasing. From electrical resistivity and Seebeck coefficient could be calculated thermoelectric power factor of Sb-doped ZnO thin films about 3.09×10^{-6} W m^{-1} K^{-2}, 9.34×10^{-7} W m^{-1} K^{-2} and 9.85×10^{-8} W m^{-1} K^{-2} for deposition time 30, 45 and 60 min, respectively.

However, the power factor of Sb-doped ZnO thin films yielded lower than that Sb-doped ZnO micro/nanobelts (3.2×10^{-4} W m^{-1} K^{-2}) [9] and metal transition doping such as; Al-doped ZnO thin film (7.63×10^{-6} W m^{-1} K^{-2}) [7].

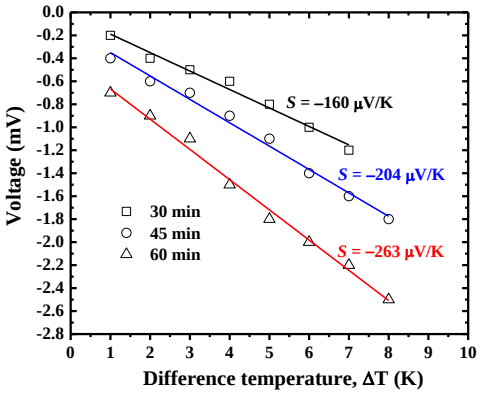

Fig. 4 Voltage and temperature difference to be obtained Seebeck coefficient of the Sb-doped ZnO thin films.

CONCLUSION

Sb-doped ZnO thin film can be prepared by DC magnetron sputtering system. The affected of deposition time can be changed shape and size of thin film crystalline. Minority of Sb doping can be enhanced of thermoelectric properties of ZnO for n-type. At room temperature, maximum thermoelectric power factor of Sb-doped ZnO thin films yielded 3.09×10^{-6} W m^{-1} K^{-2} at deposition time 30 min.

REFERENCES

[1] Y. Atsushi, I. Katsuya, M. Kei-ichiro, M.Toshihiro, Crystal and electronic band structures of homologous compounds $Zn_kIn_2O_{k+3}$ by Rietveld analysis and first-principle calculation, Mater. Res. Bull. 44 (2009) 432–436.

[2] Q. Xiurong, W.X. Wen, L. Shuchen, J.Dechang, Thermoelectric properties and electronic structure of Al-doped ZnO, Solid State Commun. 151 (2011) 332–336.

[3] X. P. Mele, S. Saini, H. Honda, K. Matsumoto, K. Miyazaki, H. Hagino, A. Ichinose, Effect of substrate on thermoelectric properties of Al-doped ZnO thin films, Appl. Phys. Lett. 102 (2013) 253903–4.

[4] J. Perrenoud, L. Kranz, S. Buecheler, F.Pianezzi, A.N. Tiwari, The use of aluminium doped ZnO as transparent conductive oxide for CdS/CdTe solar cells Thin Solid Films 519 (2011) 7444–7448.

[5]S.M. Choi, K.H. Lee, C.H. Lim, W.S. Seo, Oxide-based thermoelectric power generation module using p-type $Ca_3Co_4O_9$ and n-type $(ZnO)_7In_2O_3$ legs. Enrg. Convers. Manage. 52 (2011) 335–339.

[6] X.Q. Meng, W. Zhen, J.P. Guo X.J. Fan, Structural, optical and electrical properties of ZnO and ZnO-Al_2O_3 films prepared by dc magnetron sputtering, Appl. Phys. A 70 (2000) 421–424.

[7] A. Vora-ud, T. Seetawan, W. Somkhunthot, N. Pimpabute, T. Burinprakhon, Investigation on the enhancement of the thermoelectric power factor of ZnO thin films by Al-doping using asymmetric bipolar pulsed-DC magnetron sputtering technology, Enrg. Proc. 61 (2014) 2355–2358.

[8] A. Vora-ud, M. Horprathum, P. Eiamchai, P. Muthitamongkol, B. Chayasombat, C. Thanachayanont, A. Pankiew, A. Klamchuen, D. Naenkieng, T. Plirdpring, A. Harnwunggmoung, A. Charoenphakdee, W. Somkhunthot, T. Seetawan, Thermoelectric properties of c-$GeSb_{0.75}Te_{0.5}$ to h-$GeSbTe_{0.5}$ thin films through annealing treatment effects, J. Alloys Compd. 649 (2015) 380–386.

[9] Y. Yang, K.C. Pradel, Q. Jing, J.M. Wu, F.Zhang, Y. Zhou, Y. Zhang, Z.L. Wang, Thermoelectric Nanogenerators Based on Single Sb-Doped ZnO Micro/Nanobelts, ACSNANO 6 (2012) 6984–6989.