ภาคผนวก

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นำเสนอและตีพิมพ์ผลงานวิจัยในระดับชาติและนานาชาติ

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1. Rungrat Nontra-udorn, Athorn Vora-Ud, Somporn Thaowankaew, **Watchara Chao-moo**, Pennapa Muthitamongkol, Chanchana Thanachayanont,Suvich Samapisut, Tosawat Seetawan “Thermoelectric Properties of Sb-doped ZnO Thin Film” SACT2016.
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Effect of Annealing Treatment on Thermoelectric Properties of Ti-doped ZnO Thin Film

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Abstract. Ti-doped ZnO thin film on the glass substrate was synthesized by a dc magnetron sputtering system. A target in diameter of 60.0 mm and thickness of 3.0 mm was prepared by solid-state reaction (SSR) method from TiO_2 and ZnO powders, then the Ti-containing confirmed by X-ray diffraction (XRD) technique. The deposition condition was under base pressure at 4.67×10^{-3}Pa, operated at the pressure of 2.13 Pa, electrical current and voltage sputtering approximate of 120 mA and 500±5 V, respectively. The deposition time of 5 min was controlled the film thickness fixed around 100 nm. After deposition, the thin film samples were annealed at 373, 473 and 573 K for 60 min under a vacuum state. Phase identification, film thickness, Seebeck coefficient and electrical resistivity of as-deposited and annealed thin films were carried by the XRD technique, Tolansky method, steady-state method and Van der Pauw four-point probe method, respectively. It was found that the XRD results showed the thin film was crystal structure of ZnO at (200) peak preferred orientations. Base on thermoelectric properties, all samples displayed the n-type thermoelectricity. The effect of annealing treatment could be enhanced the power factor of Ti-doped ZnO thin film to be achieved a high power factor about of 0.76 $\mu Wm^{-1}K^{-1}$ for annealed thin film 473 K, at room temperature.

INTRODUCTION

Today, thermoelectric (TE) oxide materials are improved to be high performance for providing to devices and their applications. Because TE oxides are stable in ambient conditions [1], good thermal stability at high temperature and free of toxic elements [2]. Which, the high performance of TE materials are semiconductors must contain Bi, Pb, Sb, or Te heavy elements within mostly toxic [3-6]. The performance of thermoelectric materials can find that from the dimensionless figure of merit (*ZT*), which $ZT = S^2T/\rho\kappa$, where S, ρ, T and κ are the Seebeck coefficient, electrical resistivity, absolute temperature, and thermal conductivity, respectively. Based on high-efficiency performance TE oxide materials at a high temperature such as; p-type $Ca_3Co_4O_9$ (p-CCO) [7-9] and n-type $CaMnO_3$ (n-CMO) [10] materials for electrical generating [11] were presented. Other oxide materials were a candidate to n-type TE materials such as ZnO because it is a promising high *ZT* material due to its high melting point, low electrical resistivity and high Seebeck coefficient [12]. Moreover, it is interested in suitable doping with the transition metal or material as a same wideband semiconductor to excellent properties and attracted on either single material such as; ZnO-TiO_2 composites [13] to be reduced the electrical resistivity. Various metals such as; Al [14], Cu [15] and Ga [16], etc., have been reported for doping ZnO. In addition, titanium (Ti) has been reported to more suitable for ZnO doping [17] because the ionic size (Ti^{+4}) smaller than that of Zn^{+2} [18], which facilitates its incorporation within ZnO crystal lattice [19] without any structural defects.

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In this work, we will be reported the Ti-doped ZnO target to be deposited the thin films with a dc magnetron sputtering system. The crystalline phase, film thickness, electrical resistivity and Seebeck coefficient of Ti-doped ZnO thin films were investigated within the annealing treatment affected.

MATERIAL AND METHOD

Ti-doped ZnO thin films were synthesized by a dc-magnetron sputtering system onto the soda-lime glass substrate using a handmade Ti-doped ZnO target. A sputtering target was synthesized by SSR method from TiO_2 (99.0%, Ajax Finechem) and ZnO (99.0%, QRëC^{TM}) powders to be mixed within a Ti 1.0% : ZnO ratio. After that, the precursor powder was pressed to a pellet for 60 mm of diameter and 3.0 mm of thickness within a metal mold for 240 MPa. Then, a pellet was sintered at temperature 973 K in air for 5 hr to be obtained the Ti-doped ZnO target, which it was loaded to target holder in a vacuum chamber. Moreover, the sintering temperature has investigated from 573 K to 1073 K within phase identification carried by X-ray diffraction technique (XRD6100-Shimadzu, Japan) to be confirmed a suitable temperature. Before thin film deposition process, all glass substrates were cleaned with acetone in the ultrasonic washer for 10 min followed by drying in air, then loaded to substrate holder with the distance from sputtering target about of 5.0 cm. Next step, the target was pre-sputtered for 10 min to be removed the contaminants. The thin films deposition condition was showed in Table 1, composed of base pressure about 3.2×10^{-5} Torr from adding a turbo molecular pump (UTM 50, ULVAC), working pressure under Ar (99.99 % purity) atmosphere as flow rate 17 sccm to be obtained 1.7×10^{-2} Torr and deposition time for 5 min. Sputtering power source was applied by a dc power supply (GPR-100H05D, GWINSTEK) with the dc current of 120±5 mA and voltage of 650±5 V. After thin film deposition, as-deposited thin film samples were annealed at temperature 373 K, 473 K and 573 K, each for 1 hr.

TABLE 1. Condition sputtering Ti-doped ZnO

Base pressure (Torr)	3.2×10^{-5}
Ar flow rate (sccm)	17
Work pressure (Torr)	1.7×10^{-2}
Deposition time (min)	5
Substrate	Soda-lime glass
Annealing temperature (K)	373, 473, 573
Annealing time (min)	60

As-deposited and annealed thin films were observed phase identification by XRD and film thickness (t) by in-house-built film thickness measurement based Tolansky method [20] using a Na-monochromatic lamp within a wavelength of 590 nm. In addition, film thickness has been obtained from the cross-section images as observed by scanning electron microscope (SEM) to be confirmed the measuring results. Note that, the film thickness is of very important to be obtained the electrical resistivity (ρ) as measured by Van der Pauw four-point probe method as followed;

$$\rho \approx \frac{\pi t}{\ln 2}\left[\frac{R_{\mathrm{AB,CD}} + R_{\mathrm{BC,DA}}}{2}\right] \tag{1}$$

where R and t are the resistance and film thickness with controlled (~100 nm), respectively. Seebeck coefficient was measured by in-house-built Seebeck apparatus [21] using the difference temperature (ΔT) and voltage (ΔV) during the heat flow as expressed $S = \Delta V/\Delta T$. The power factor (P) of thin films was calculated from the measured values of S and ρ using the expression $P = S/\rho$.

RESULTS AND DISCUSSION

Figure 1 shows the XRD peaks of the Ti-doped ZnO target after sintered at temperature 973 K within majority peak of ZnO and contained with Ti (100) peak as confirmed by PDF# 891397 and PDF# 892762 for ZnO hexagonal wurtzite structure and Ti phases, respectively. The target of pre-sputtered was illustrated in Fig. 1. After deposition, as-deposited and annealed thin films were crystallinity of the ZnO (002) single peak without phase corresponding to the Ti dopants as shown in Fig. 2. This case can be suggested in two reasons; 1) the either Ti may be replaced Zn in the hexagonal lattice or 2) Ti segregated to the nation-crystalline region at the grain boundary [22]. In addition, the crystal size (D) and lattice stain (ε) as shown in Fig.3, are evaluated from the full width at half maximum (FWHM) using Debye-Scherrer's formula;

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{2}$$

and

$$\varepsilon = \frac{\beta}{4\tan\theta} \tag{3}$$

where K, λ, β and θ are the shape factor (0.9), the wavelength of CuK$_\alpha$ radiation, the line broadening at FWHM and diffraction angle, respectively. The FWHM values were obtained via PCXRD software Ver. 7 (SHIMADZU) based on Williamson–Hall (W–H) analysis.

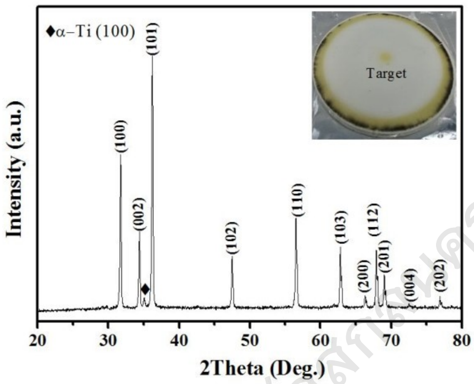

FIGURE 1. XRD result of Ti-doped ZnO target (ZnO: pdf# 891397) and (Ti: pdf# 892762).

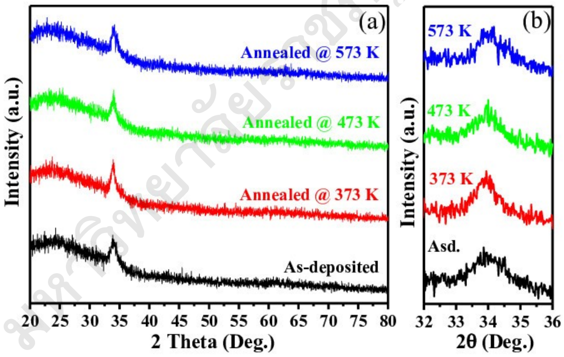

FIGURE 2. (a) XRD pattern of Ti-doped ZnO thin film samples with difference annealing temperature and (b) enlarge for analysis FWHM of the (002) peak.

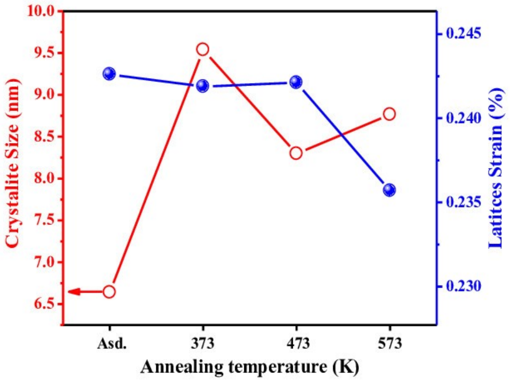

FIGURE 3. The crystal size and lattice strain of Ti-doped ZnO thin film samples with difference annealing temperature.

From Fig. 3, the crystal size of Ti-doped ZnO thin films has been tended to increase with the annealing temperature increasing while lattice strain was decreased with the annealing temperature increasing. These results can be supported by the two reasons as mentioned for Ti and Zn relationship [22]. Also, this work can be controlled by the film thickness about of 100 nm as confirmed by cross-section SEM images in Fig. 4.

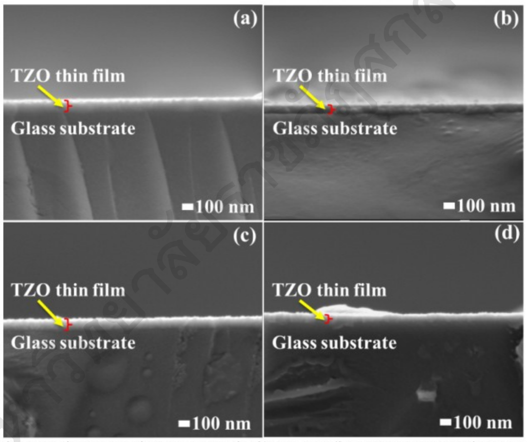

FIGURE 4. Cross-section SEM images of Ti-doped ZnO thin film at annealing temperature function (a) as-deposited, (b) 373 K, (c) 473 K and (d) 573 K.

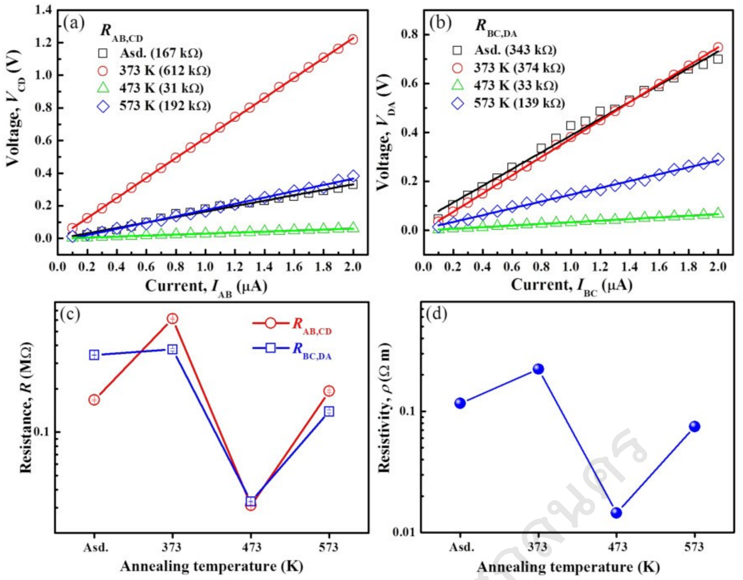

FIGURE 5. Electrical properties measurement of Ti-doped ZnO thin film samples with difference annealing temperature (a) I_{AB}-V_{CD} characteristic, (b) I_{BC}-V_{DA} characteristic, (c) resistance of $R_{AB,\,CD}$ and $R_{BC,\,DA}$ and (d) electrical resistivity.

Figure 5 shows the electrical properties measurement to be evaluated the electrical resistivity of Ti-doped ZnO thin film samples with the annealing temperature function. The last section, Seebeck coefficient measurement and power factor calculation of Ti-doped ZnO thin film samples with difference annealing temperature as shown in Fig. 6. The sign of Seebeck coefficient showed minus values to be found in the n-type thermoelectricity. Note that, at room temperature, the maximum power factor of Ti-doped ZnO thin film achieved from this study is around 0.76 μWm^{-1}K^{-1} for the annealed thin film at 473 K due to lowest electrical resistivity and high Seebeck coefficient.

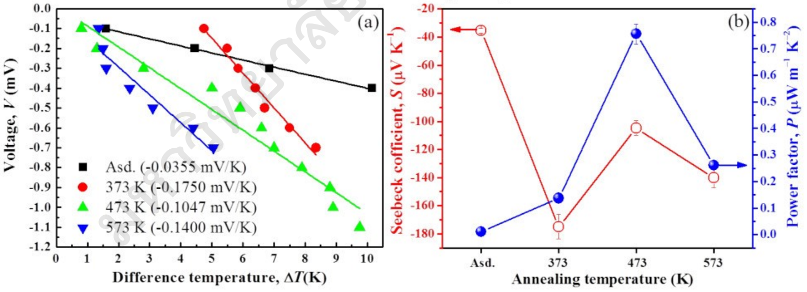

FIGURE 6. (a) Seebeck coefficient measurement and (b) Seebeck coefficient and power factor of Ti-doped ZnO thin film samples with difference annealing temperature

CONCLUSION

Ti-doped ZnO thin film could be successfully synthesized onto the glass substrate by a local dc-magnetron sputtering system and low-cost target. All Ti-doped ZnO thin films samples showed hexagonal wurtzite structure with the (200) single peak and the n-type thermoelectricity. At annealed temperature 473 K, Ti-doped ZnO thin film was lowest electrical resistivity, high Seebeck coefficient and maximum power factor approximately 1.45×10^{-2} Ω m, 104.7 μV K^{-1} and 0.76 μW $m^{-1}K^{-1}$ at room temperature, respectively.

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