Fabrication of Al-doped ZnO thin films through ink-jet printing

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ABSTRACT

Al-doped ZnO thin films were prepared by ink-jet printing through aqueous solutions of zinc nitrate and aluminium nitrate. Different ratios of Al-doped ZnO thin films were obtained through ink-jet printing method where a minimum 50 print cycles were required for continuous films. The Al-doped ZnO thin films were sintered at temperature 300 °C. The thickness of the Al-doped ZnO thin films was not significantly change by increasing the Al-doped ratio where the thickness had an average 8.5µm. The electrical conductivity of Al-doped ZnO thin films was increased from 4.5 S/cm to 114.1 S/cm as the Al-doped ratio increased from pure ZnO to 4% Al-doped respectively. The pure ZnO sample posses a high Seebeck coefficient at room temperature about -17.63 µV/K and the values decreases to -15.11µV/K and -14.35µV/K when the Al-doped ratio increased to 3wt% and 4wt% Al-doped respectively. It shows that the efficiency of thermoelectric properties of ZnO improved with Al-doped since it had low thermal conductivity and high electrical conductivity as the amounts of Al-doped increased.

Keywords: Al-doped ZnO, Thin films, Electrical conductivity, Seebeck coefficient.

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INTRODUCTION

Ink-jet printing process is a contactless technique of printing and widely used for desktop publishing. The inkjet printing had been applied as alternative way for producing microcircuits and metallization of solar cell due to the low cost of fabrication [1,2]. The advantages of inkjet printing include low cost, easy to control, direct patterning and low wastage [3]. Doped zinc oxide thin films have been widely studied for their application as conducting electrode materials in flat-panel displays or solar devices. Unlike the more commonly used indium tin oxide (ITO), zinc oxide is a non-toxic and inexpensive material. Furthermore, it is II-VI n-type semiconductor with band gap of approximately 3.3 eV at room temperature and a hexagonal wurtzite structure [4].

Thermoelectric performance and efficiency of zinc oxide is quite low [5]. The conversion efficiency of thermoelectric material depends on the thermoelectric figure of merit (ZT) of the material properties [6]. The thermoelectric figure of merit defined as ZT=σS2/λ, where S is the Seebeck coefficient, σ is the electrical conductivity and λ is the thermal conductivity. There were three requirements of physical properties for thermoelectric materials based on Equation 1 to improve the efficiency of thermoelectric properties of the materials, [7]. The materials need to be low thermal conductivity (λ), which is necessary to introduce a large temperature difference into both ends of the material. Besides, it needs to be high electrical conductivity (σ), which is required to reduce the internal resistance of the material. The material should have large thermoelectromotive force (Seebeck coefficient, S), which is needed to obtain a high voltage.

Among the zinc oxide films doped with group II elements such as barium, aluminum, gallium and indium, aluminum-doped zinc oxide (AZO) thin films show the lowest electrical resistivity[8]. Doping is the influence factor to improve the thermoelectric performance of the existing materials. It is well known that the addition of doping is a feasible route to optimizing the thermoelectric performance. In the present work, the effects of Al doping on the Seebeck coefficient and physical properties of ZnO are investigated. Xiurong et al [9] reported that with Al doping ZnO, the electrical conductivity increases and the thermal conductivity decreases significantly, where the Seebeck coefficient decreases slightly. In the present work, the fabrication of thin films through ink-jet printing and the effects of Al-doped on the thermoelectric and structural properties of ZnO thin films are investigated.

MATERIALS AND METHODS

Al doped ZnO film samples were obtained through inkjet printing process. Appropriate amounts of 0.4 M $Al(NO_3)_3$ solution and 0.4 M $Zn(NO_3)_2$ solution were prepared. The solution was injected into the empty ink cartridge of the printer (Canon pixma iP4810, Japan) for printing process. The ZnO film doped with 1%, 2%, 3% and 4% of Al were printed out through the inkjet printer with glass as substrates. Several print cycles were repeated to obtain visually homogeneous films. The morphology of films was observed through optical microscope. After printing, the samples were sintered at 300 °C for 2 hours with heating and cooling rate of 10 °C/min. A sample with no Al additive was sintered under the same condition with the doped one as a reference for thermoelectric characterization.

The synthesized samples of Al-doped ZnO thin films were characterized by X-ray diffraction analysis (Shinadzu XRD 2000). The thickness of Al-doped ZnO thin films were estimated by cross section view using scanning electron microscope (SEM JEOL JSM-6460 LA Jeol Japan). The electrical conductivity was measured through a conventional two probe method at room temperature. The Seebeck coefficients were measured through a differential method [10] at room temperature. The Seebeck coefficient was calculated from the equation $S=\Delta V/\Delta T$. The Seebeck coefficient was calculated from the relation between the ΔV and ΔT, where ΔV is voltage generated between both ends of specimen across various temperature differences, ΔT was applied.

RESULTS AND DISSCUSION

Fig 1 shows the XRD spectra of Al-doped ZnO thin films sintering at temperatures 300 °C with different percentage of Al-doping from 1wt% to 4 wt%. The peaks are identified as the plane reflections for wurtzite phase of zinc oxide according to the standard JCPDS data file (No. 36-1451), impurity peaks were not detected. The crystalline orientations of the films were similar to the previous work done by Yu-Yun Chen et al [11].They found the peaks (002) of the phase ZnO correspond to the standard JCPDS data file (No. 36-1451).The doped materials did not form significant amounts of additional crystalline phases since no additional peaks were found. There was no change in the peak intensity and position with increasing the percentage of Al-doped.

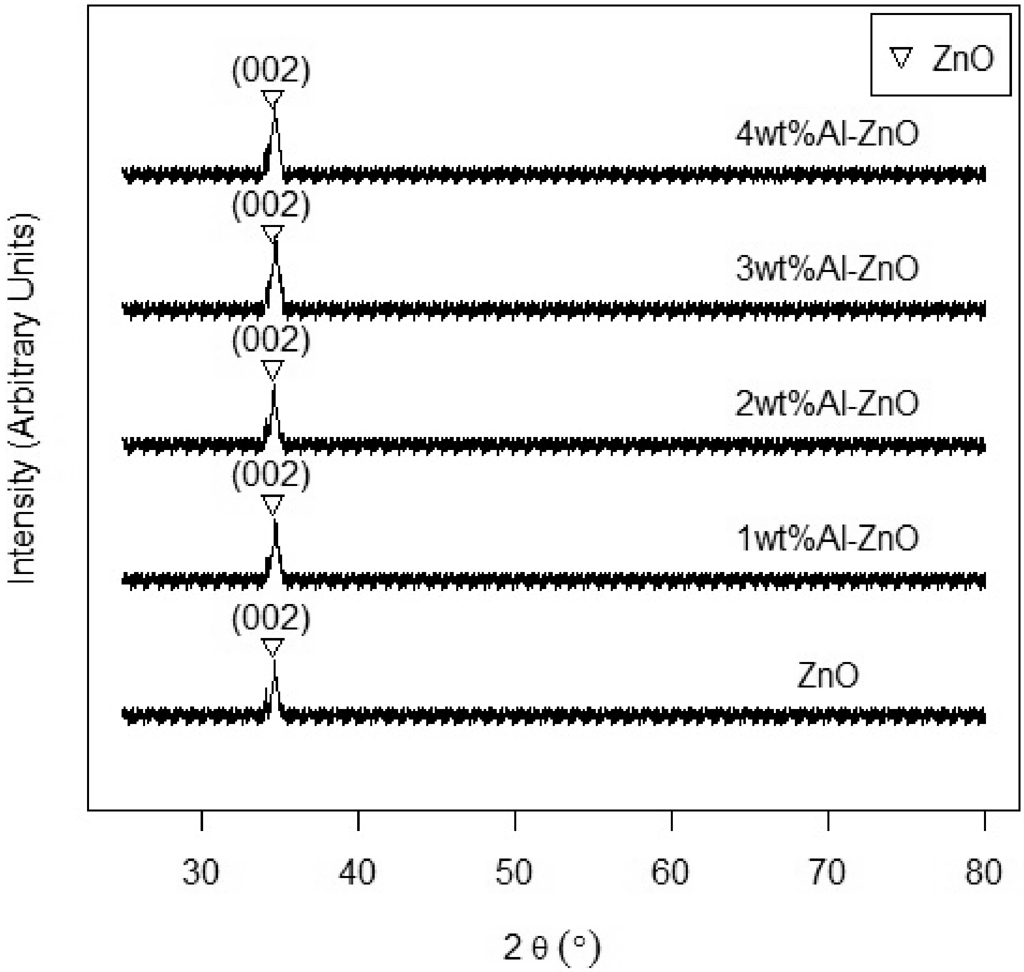

Fig. 1: X-ray diffraction pattern of Al-doped ZnO with percentage of Al-doped.

The thickness of the Al-doped ZnO thin films with different percentage of Al-doping are summarized in Table 1. Based on the results, the different percentage of Al-doped ZnO did not have a significant effect to the thickness of thin films. The thickness of different Al-doped ZnO thin films are similar. S. Mondal et al [12] studied the thickness thin films for pure ZnO and Al-doped ZnO. They found that with the increasing percentage of Al-doped does not influence the thickness of the thin films where there were no significant change in thickness between the pure ZnO and Al-doped ZnO thin films. This is similar to the results of experiment. It shows that change in thermoelectric properties of Al-doped thing films might not due to the thickness of thin films and it possibly due to the Al-doping.

Table 1. Thin films thickness measurement.

No	Thin films thickness (µm)				
	ZnO	1% Al-doped ZnO	2% Al-doped ZnO	3% Al-doped ZnO	4% Al-doped ZnO
1	8.62	8.48	8.56	8.61	8.57
2	8.46	8.67	8.64	8.52	8.63
3	8.71	8.58	8.49	8.65	8.49

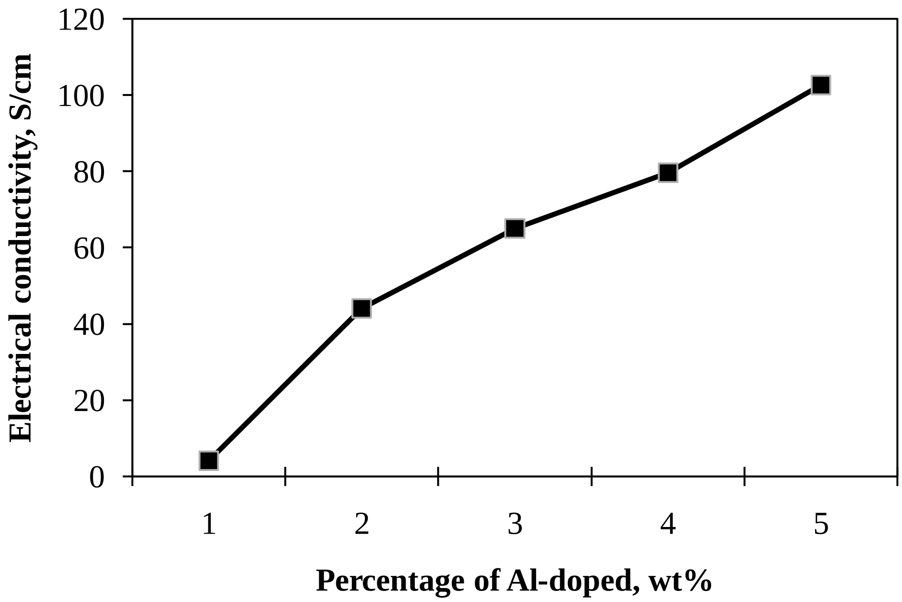

Fig. 2: Electrical conductivity of Al-doped ZnO with different percentage of Al-doped.

The effect of Al doping was significantly shown in thermoelectric properties. Figure 2 shows the electrical conductivity of Al-doped ZnO with different amount percentage of Al-doped. The results showed that the electrical conductivity of the thin films was significantly increased from 5 S/cm to 114 S/cm with increasing the Al-doped concentration from pure ZnO to 4% Al-doped respectively. The transport properties of ZnO were changed from semiconducting to metallic by Al-doped. Since ZnO had a low electrical conductivity [9], the increasing of electrical conductivity might probably caused by some Al dissolved in the ZnO crystal lattice acts as donor [10]. The electrical conductivity was improved drastically by doping Al into ZnO.

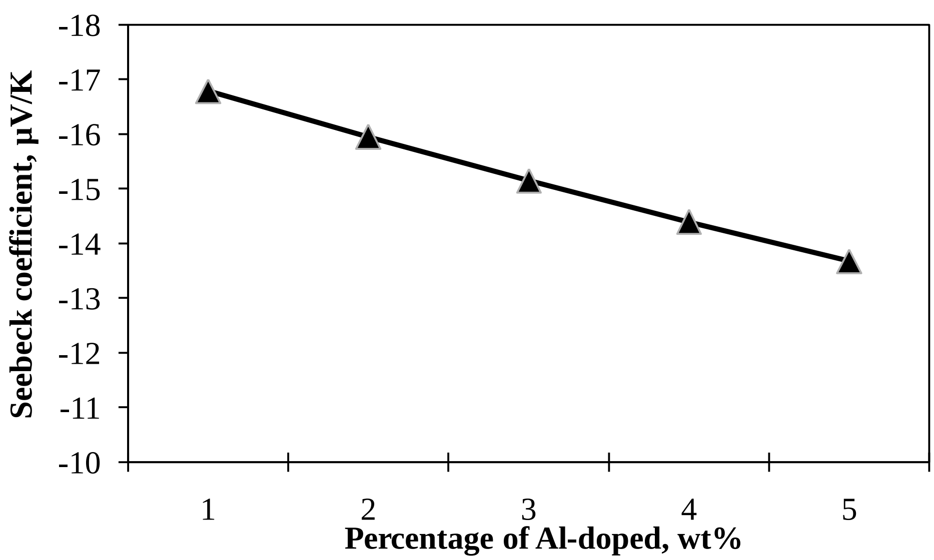

Fig. 3: Seebeck coefficient of Al-doped ZnO with different percentage of Al-doped.

Fig 3 shows the Seebeck coefficient of Al-doped ZnO thin films with different amount of Al-doped and sintering temperature. The negative sign of the Seebeck coefficient indicated the sample as the n-type semiconductor. It can be seen from the results that the Seebeck coefficient slightly decreased with the increase of Al-doped concentration from 1wt% to 4wt%. The pure ZnO sample posses a high Seebeck coefficient at room temperature about -17.63 µV/K and the values decreases by Al-doping. The Seebeck coefficient decreased to -15.11µV/K and -14.35µV/K when the sample added 3wt% and 4wt% Al-doped respectively The Seebeck coefficient was slightly decreases by Al-doped into ZnO [6].

CONCLUSION

Al-doped ZnO thin films had been prepared through ink-jet printing method with $Al(NO_3)_3$ solution and $Zn(NO_3)_2$ solution as starting materials. The thermoelectric properties of Al-doped ZnO were evaluated in room temperature. The Al-doped ZnO thin films printed on glass substrate was observed through optical microscope where a minimum 50 print cycles was required to obtain continuous films. The electrical conductivity was improved by more than two orders of magnitude by increased the amount of Al-doped into ZnO. The Seebeck coefficient at room temperature was slightly reduced as the amount of Al-doped increased. The efficiency of thermoelectric properties of ZnO improved with Al-doped since it had high electrical conductivity as the amounts of Al-doped increased. Conclusively, high electrical conductivity (σ) was obtained by Al-doped, which is required to reduce the internal resistance of the material.

REFERENCES

[1] H. Sirringhaus, T. Kawase, R. H. Friend. High-resolution ink-jet printing of all-polymer transistor circuits. *MRS Bulletin*, Vol. 26(7), pp. 539-543,2001.

[2] K. F. Teng, R. W. Vest. Liqiud Ink Jet Printing with Mod Inks for Hybrid Microcircuits. *IEEE Transactions on Components, Hybrids and Manufacturing Technology*, Vol. CHMT-10(4), pp. 545-549,1987.

[3] Yuming Ai, Yi Liu, Tianhong Cui, Kody Varahramyan Thin film deposition of an n-type organic semiconductor by ink-jet printing technique. *Thin Solid Films*, Vol. 450 (2), pp. 312-315,2004.

[4] Nolas, G.S., Sharp, J., Goldsmid, H.J. Thermoelectrics : basic principles and new materials developments. *Berlin ; London, Springer*, 2001.

[5] S. J. Pearton, D. P. Norton, K. Ip, Y. W. Heo, and T. Steiner. Recent progress in processing and properties of ZnO. *Superlattices and Microstructures*,Vol. 34, pp.3-32,2003.

[6] C. Godart, Gonçalves, E. B. Lopes, B. Villeroy. Role of Structures on Thermal Conductivity in Thermoelectric Materials. *In Properties and Applications of Thermoelectric Materials*, pp. 19-49, 2009.

[7] David M. Rowe. CRC handbook of thermoelectrics. *CRC Press*, 1995.

[8] Y. Igasaki, H. Saito The effects of deposition rate on the structural and electrical properties of ZnO:Al films deposited on (112-bar 0) oriented sapphire substrates. *Journal of Applied Physics*, Vol. 70(7), pp. 3613-3619,1991.

[9] Xiurong Qu, Wen Wang, Shuchen Lv, Dechang Jia. Thermoelectric properties and electronic 0f Al-doped ZnO. *Solid State Communications* Vol.151, pp. 332-336,2011.

[10] D. Ravinder. Thermoelectric power studies of zinc substituted copper ferrites. *Journal of Alloys and Compounds* Vol.291, pp. 208–214,1991.

[11] Yu-Yun Chen, Jin-Cherng Hsu, Paul W. Wang, Yao-Wei Pai, Chih-Yuan Wu, Yung-Hsin Lin. Dependence of resistivity on structure and composition of AZO films fabricated by ion beam co-sputtering deposition. *Applied Surface Science* Vol.257, pp.3446–3450,2011.

[12]S. Mondal . Preparation of al-doped ZnO (AZO) thin film by SILAR. *Journal of Physical Sciences*, Vol.12,pp.221-229,2009.