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Investigation on the Enhancement of the Thermoelectric Power Factor of ZnO Thin Films by Al-doping using Asymmetric Bipolar Pulsed-DC Magnetron Sputtering Technology

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Abstract

ZnO and Al-doped ZnO thin films were deposited on ceramic substrate by using an asymmetric bipolar pulsed-DC magnetron sputtering system under Ar atmosphere. Compacted ZnO powder and ZnO:Al_2O_3 premixed powder in copper supports were used as sputtering targets for the deposition of ZnO and Al-doped ZnO thin films, respectively. Optical emissions from the plasma during the deposition, measured using a high resolution spectrometer in the wavelength range of 360-800 nm, showed that the constituents of each target were successfully sputtered off. X-ray diffraction (XRD) analysis confirmed the formation of ZnO and Al-doped ZnO thin films of hexagonal crystal structure. The deposition rates of 24 and 15 nm/min were obtained for the ZnO and Al-dopoed ZnO thin films, respectively. The electrical conductivity and Seebeck coefficient of the thin films were measured at room temperature by the steady state and the Van der Pauw four probe methods, respectively. The increase in thermoelectric power factor of about 2 orders of magnitude was observed for the Al-doped ZnO thin films.

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Keywords: Al-doped ZnO thin films, electrical conductivity, pulsed-dc magnetron sputtering

1. Introduction

Zinc oxide (ZnO) is one of the wide band gap semiconductors of great interest [1-2]. It is versatile for numerous commercial applications, for example, as an additive in various industrial products ranging from plastics, ceramics, glass, cement, rubber, lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries,…, to first aid tapes. In addition, ZnO has been attractive as an alternative window material for solar cells [3] and thermoelectric element for thermoelectric generators [4]. These devices have been recognized as promising technologies for clean energy production. In the latter, good thermoelectric materials are required. This is usually evaluated by the dimensionless figure of merit (*ZT*)

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$$ZT = \frac{S^2 \sigma T}{\kappa} \quad (1)$$

where S, σ, κ and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. ZnO gives S as high as -200 μVK^{-1} [2] but has very low σ (order of 10^{-3} Sm^{-1}) [2, 5] so that its thermoelectric power factor (P) is rather low, leading to poor thermoelectric performance following by Eq. (2)

$$P = S^2 \sigma \quad (2)$$

One way to improve ZnO thermoelectric power factor is to boost its electrical conductivity while keeping the reduction of the Seebeck coefficient to minimal. It has been found that dc-magnetron sputtered ZnO-Al_2O_3 thin films exhibit electrical conductivity of seven order of magnitude as high as that of pure ZnO, due to Al-doping into the ZnO grains [5]. This suggests that Al-doping can be a straight forward method for improving the thermoelectric power factor of ZnO.

In this work, the enhancing of thermoelectric power factor of ZnO thin films by Al-doping was investigated. The ZnO and Al-doped thin films were deposited by using the asymmetric bipolar pulsed-DC magnetron sputtering technology. The results of plasma diagnostic during deposition process, crystal structure and elemental composition analysis, and the electrical conductivity and Seebeck coefficient measurements at room temperature of the as-deposited films are reported.

2. Experimental Procedures

Thin films of ZnO and Al-doped ZnO were prepared by an in-house-built asymmetric bipolar pulsed-dc magnetron sputtering system [6]. The sputtering target, 60 mm in diameter and 3.0 mm thick, for the deposition of pure ZnO films was made from ZnO powder (99.99 %, QRëC, New Zealand) compacted in a copper supporting cap at pressure of 70 MPa. For Al-doping, a premixed powder ZnO+Al_2O_3 was used instead of pure ZnO. The premixed powder was prepared by mixing ZnO (99.99 % , QRëC, New Zealand) and Al_2O_3 (99.99%, Aldrich-Sigma, Germany) powders with ball milling method for 10 hr, followed by thermal annealing at 973 K in air for 4 hours. The used mixing ratio was to give the nominal composition Zn:Al of the target to be 1:0.01. The thin films were deposited under argon atmosphere of 9.33 Pa onto ceramic substrates made of clay and Al_2O_3 composites with the deposition times of 40 minutes. The target-to-substrate was 5.0 cm, and no additional heating was applied to the substrates. The pulsed-dc power applied to the targets was operated at approximately 17 kHz, with the sputtering on-time (negative voltage pulse width) of 20 μs, the reverse sputtering on-time (positive voltage pulse width) of 10 μs, and the pulse off-time of 14 μs. The negative voltage pulse/current at the target were 650±30 V/100 mA, and 600±30 V/120 mA for the ZnO and ZnO+Al_2O_3 targets, respectively. The positive voltage pulse (+V) was set at 100±10 V for both targets.

The optical emissions from plasma during sputter deposition of films were observed in the wavelength range of 360-800 nm using a high resolution spectrometer (the getSpec-2048 spectrometer, Sentronic GmbH). The spectral lines were indexed to the Atomic Spectra Database [7]. Identifying the phases of as-deposited films was performed by X-ray diffraction measurement using the X-ray diffractometer (XRD-6100, Shimadzu). The thickness and surface morphology of the as-deposited films were analysed by the scanning electron microscope (SEM, JSM-5410, JEOL). The Seebeck coefficient and electrical conductivity of the as-deposited films were measured by the standard steady state and four probe Van der Pauw methods, respectively [8].

3. Results and Discussion

The optical emissions from the plasma during the sputtering of the ZnO and ZnO+Al_2O_3 targets are illustrated in Fig.1. The spectra show that the atomic constituents of each target are successfully sputtered. Hence, we can expect that the deposited films will contain Zn and O, and Zn, O, and Al for the ZnO and ZnO+Al_2O_3 targets, respectively. Figure 2 shows the XRD patterns of the as-deposited ZnO and ZnAlO thin films. The majority of peaks in the patterns are from the substrate contributions, including Al_2O_3,

SiO_2, SiC phases. However, the peaks at 2θ=31.7°, 34.4°, 36.2°, 56.5°,62.7° and 66.3° are matched to those of ZnO of hexagonal wurtzite structure (JCPDS: 89-1397). In addition, there is no trace of free metallic Al in the patterns. This indicates that ZnO and Al-doped ZnO thin films were successfully deposited on the substrates, as can be seen in the SEM images in Fig.3. The XRD patterns also suggest that the deposited films exhibit the [002] preferred orientation. The thickness estimated from the cross section SEM images, electrical conductivity, Seebeck coefficient and thermoelectric power factor of the as-deposited ZnO and Al-doped ZnO thin films are shown in Table 1. The deposition rates of the ZnO and Al-doped ZnO thin films are 28 and 15 nm/min, respectively. The lower deposition rate of Al-doped ZnO thin films is likely due to the lower sputtering yield of the ZnO+Al_2O_3 than that of pure ZnO. The electrical conductivity of the Al-doped ZnO thin films is 264 times as high as that of ZnO films while the Seebeck coefficient of the Al-doped ZnO thin films decreases by less than one order of magnitude, as compared to that of the ZnO films. As a result, the increase in the thermoelectric power factor of about 233 times is obtained for the Al-doped ZnO thin films. The thermoelectric power factor of the investigated Al-doped ZnO is comparable to those of other thermoelectric oxide materials [2, 9-10].

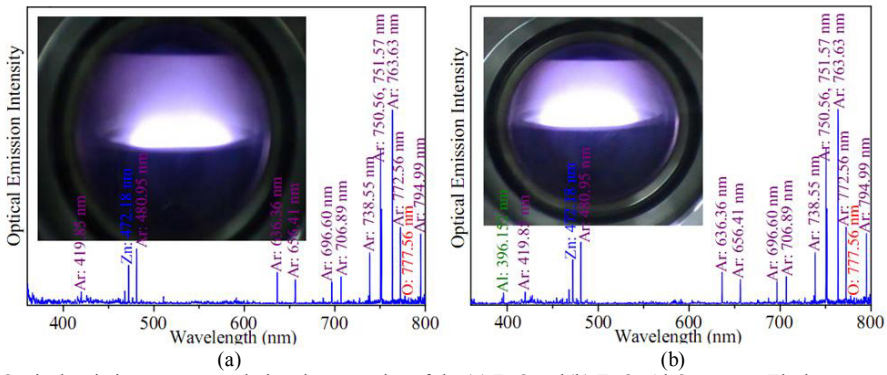


Fig. 1. Optical emission spectra are during the sputtering of the (a) ZnO and (b) ZnO+Al_2O_3 targets. The insets are the optical images of the plasma formed above the corresponding targets.

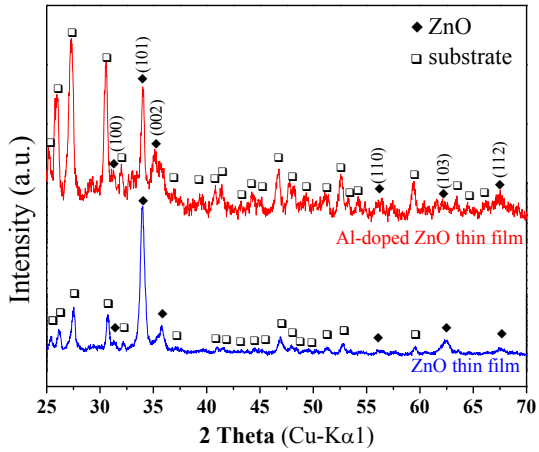
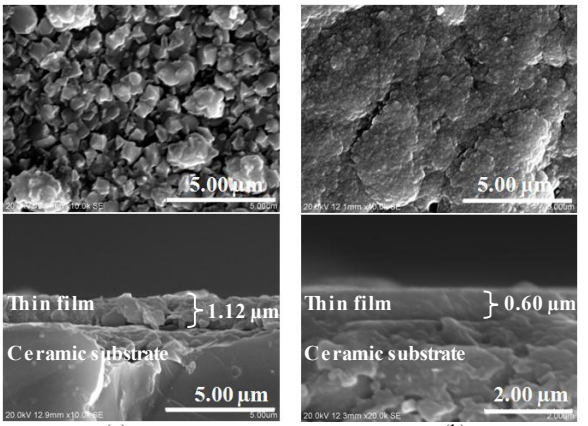


Fig. 2. XRD pattern of ZnO and Al-doped ZnO thin films on ceramic substrates at deposition times of 40 minutes

Table 1. Films thickness and thermoelectric properties and of ZnO, and Al-doped ZnO thin films

Thin films	Film thickness (μm)	σ (Sm^{-1})	*S* (μVK^{-1})	*P* (μ$Wm^{-1}K^{-2}$)
ZnO	1.12	1.03	-178.40	0.033
Al-doped ZnO	0.60	271.89	-167.53	7.631



(a) (b)

Fig. 3. SEM images (top panel: top view SEM, bottom panel: cross section view SEM) of (a) ZnO and (b) Al-doped ZnO thin films deposited on ceramic substrates at deposition times of 40 minutes.

4. Conclusions

The Al-doped ZnO thin films of hexagonal wurtzite structure were successfully deposited on Al_2O_3-clay composite substrates by using the asymmetric bipolar pulsed-DC magnetron sputtering technology. The deposited Al-doped ZnO thin films exhibit the thermoelectric power factor of about 2 order of magnitude as high as that of ZnO films, at room temperature. The thermoelectric power factor enhancement is a result of the stronger effects of the Al-doping on the increase of electrical conductivity than the reduction of the Seebeck coefficient of ZnO.

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