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Substrate temperature and background pressure effects on nanostructured zinc oxide thin films for thermoelectric applications

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Abstract

Zinc oxide (ZnO) thin films were grown on glass substrate by pulsed laser deposition (PLD) at different substrate temperature ranging from room temperature (RT) to 300°C and various oxygen background pressures ranging from 14 mTorr to 140 mTorr, respectively. The structural, surface morphology and electrical properties of the ZnO films were investigated for thermoelectric (TE) applications. It was found that all of the fabricated ZnO films are preferentially in *c*-axis (002) orientation. Results showed that the electrical conductivity increased with higher substrate temperature and higher oxygen pressure. The high conductivity can be attributed to the increased grain size and surface roughness, which consequently reduced the grain boundary scattering.

Keywords: Thermoelectric; Zinc oxide; Thin film; Pulsed laser deposition.

1. Introduction

Thermoelectric (TE) devices are able to harness heat and convert it into electricity. The TE efficiency is remain a challenge, measured by a dimensionless figure-of-merit, $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the thermal conductivity. Based on the equation, optimized combination of high S, high σ and low κ are required for obtaining superior TE materials of at least $ZT \geq 3$, in order to achieve more comparable performance with the conventional energy conversion system [1-3]. Zinc Oxide (ZnO) shows potential as a TE candidate as it exhibits high S in bulk, thermally stable, non-toxic, oxidation resistive, simple and low-costs in productions [4, 5]. Thus, in this work, substrate temperature and oxygen background pressure dependent structural, morphological and electrical properties of ZnO thin films for TE applications have been studied.

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2. Experimental

ZnO thin films were deposited on glass substrates by pulsed laser deposition (PLD). The substrates were ultrasonically cleaned in detergent, acetone, isopropyl alcohol and de-ionized water, for 10 minutes respectively and dried using nitrogen air gun. Nd:YAG pulsed laser with wavelength of 355 nm, pulse width of 4.7 ns, repetition rate of 10 Hz, and energy density of 2 J/cm^2, was used to ablate a 99.99% purity ZnO ceramic target disk. Target-to-substrate distance of 50 mm and deposition duration of 45 minutes were kept. The substrate temperature was varied in the range of 26 – 300°C at fixed oxygen pressure of 14 mTorr, and the oxygen pressure was varied in the range of 14 – 140 mTorr at fixed substrate temperature of 100°C, respectively. The structural properties of the prepared ZnO thin films were examined by X-ray diffractometer (XRD, Bruker D8 Advance) using Cu-K_α radiation with 0.15406 nm wavelength operated at 40 kV and 50 mA. The average crystalline grain size of each films were estimated using the Debye-Scherrer formula: $D = 0.9\lambda/\beta\cos\theta$, where D is the crystallite size, λ is the wavelength of Cu K_α radiation, β is the full-width at half-maximum (FWHM) of the diffraction peak in unit radians and θ is the Bragg angle [6]. The surface morphology was observed by field emission scanning electron microscope (FESEM, FEI Nova NanoSEM 450) with 200 k× magnification at 5 kV accelerating voltage and 5.1 mm working distance. The root mean square (RMS) roughness was measured by atomic force microscope (AFM, Nanosurf easyScan 2) in contact mode over 5×5 μm^2 scan size. The elemental compositions were determined by energy dispersive X-ray spectrometer (EDX, Zeiss Supra 55 VP). The electrical conductivity (inverse of electrical resistivity) was characterized by four-point probes I-V measurement system (Keithley 236) operated at supply current of 0.1 nA.

3. Results and Discussions

3.1 Substrate Temperature Effect

XRD patterns in Fig. 1 show that the ZnO thin films grown at room temperature (RT), 100, 200 and 300°C with a fixed oxygen pressure of 14 mTorr are all preferentially *c*-axis oriented, evident by the presence of significantly sharp (002) ZnO diffraction peak at 2θ of 34.4°. Since the ZnO films deposited at RT are prone to amorphous, it is interesting to note that highly crystalline ZnO film can be obtained at RT by the present PLD technique. This may be due to high-energy laser-induced plumes that favor the crystalline grain growth [7]. It can also be seen that the intensity of (002) peak decreases with substrate temperature, which means that the crystallinity of the films along the (002) plane are degraded.

Fig. 2 shows the position and FWHM of the (002) peaks extracted from the XRD spectrum. According to the JCPDS (card no. 79-0205) for ZnO, standard (002) peak position of ZnO powder occurs at 2θ = 34.421°. As compared to the bulk ZnO, the diffraction peak angles (2θ) of films grown at RT and 100°C are higher (34.5° and 34.425°). This indicates that tensile stress is induced along the interfaces of the films. Conversely, the diffraction angles of films grown at 200°C and 300°C are lower than that of bulk ZnO (34.3° and 34.325°), which implies that the films are under compressive stress. It has been reported that the compressive stress are formed with the increasing substrate temperature as a result of the lower thermal expansion coefficient of ZnO (6.5×10^{-6} °C^{-1}) than that of the glass substrate ($8–10\times10^{-6}$ °C^{-1}) [7, 8].

FWHM of the (002) peak decreases from 0.483° to 0.201° as the substrate temperature increases from RT to 300°C, whereby similar variation in FWHM has also been observed by others [6, 9]. Since the grain size is inversely proportional to the FWHM, as shown in Table 1, the calculated grain size are in incrementing trend of 17.22 nm to 41.30 nm. These results are consistent with the FESEM observations, where coarse grains are obtained at higher substrate temperature (as shown in Fig. 3), attributed mainly to the contributions of the substrate temperature on the energy of particle for mobility on the growth surface [7]. The FESEM images also show that the films are composed of homogeneous columnar ZnO grains [7, 10, 11].

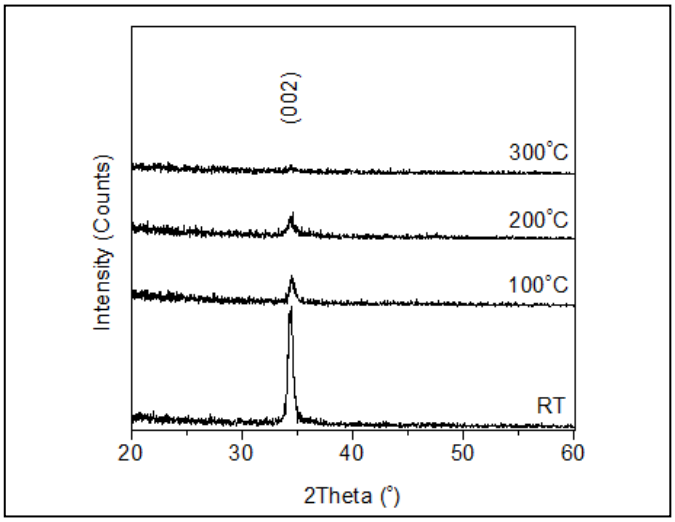

Fig. 1: XRD patterns of ZnO thin films at various substrate temperatures.

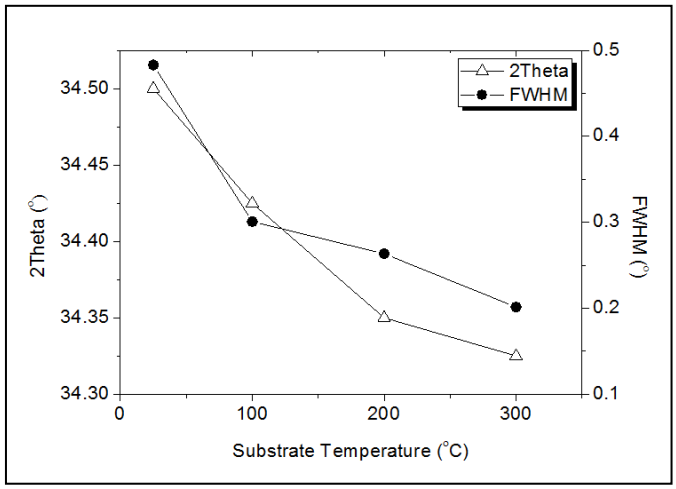

Fig. 2: Position and FWHM of (002) diffraction peak for ZnO thin films at various substrate temperatures.

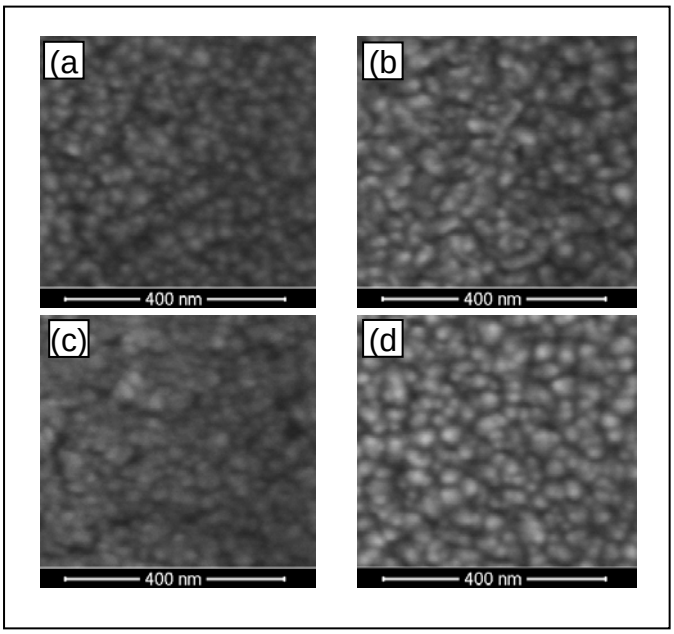

Fig. 3: FESEM images of ZnO thin films at substrate temperature (a) RT, (b) 100, (c) 200 and (d) 300°C.

Table 1: Properties of ZnO thin films at various substrate temperatures

Substrate Temperature [°C]	**Grain size (XRD) [nm]**	**Surface Roughness RMS [nm]**	**Resistivity [Ωm]**	**Conductivity [Sm^{-1}]**
RT	17.22	20.49	8.3622	0.1196
100	27.65	18.29	0.8239	1.2137
200	31.55	23.19	0.1067	9.3721
300	41.30	19.63	0.0572	17.4825

As summarized in Table 1, the surface roughness fluctuates with the increasing substrate temperature. However, it is noting that the roughness are higher (23.19 nm and 19.63 nm) for ZnO films deposited at 200°C and 300°C as compared to the films at lower temperature of RT and 100°C (20.49 nm and 18.29 nm). The increasing trend of average roughness with substrate temperature is comparable with the AFM results obtained in literature [9]. It is also shown in Table 1 that the films deposited at higher temperature possess lower electrical resistivity (or higher conductivity), correspondingly coupled to larger grain size and rougher surface. The highest conductivity of 17.4825 Sm^{-1} is recorded for film prepared at 300°C, whereby the improved conductivity is due mainly to the decreased in grain boundary scattering [12]. As the grain size grows larger (at higher substrate temperature) the grain boundaries become less, and hence, permit the electronic transport and reduce the scattering of charge carriers [13].

3.2 Background Pressure Effect

As shown in Fig. 4, only strong (002) diffraction peaks are observed in the XRD patterns for ZnO thin films deposited at oxygen background pressure of 14, 42, 84 and 140 mTorr with fixed substrate temperature of 100°C. This indicates that the films are all in good *c*-axis preferred orientation, with the exception of an additional weak (101) hexagonal ZnO reflection at 2θ = 36.3° that can be seen in the film prepared at 42 mTorr. Besides, the (002) peak intensities decrease for films prepared at higher oxygen pressure (84 mTorr and 140 mTorr) as compared to 42 mTorr, which implies that the crystallinity is low at high pressure condition [13].

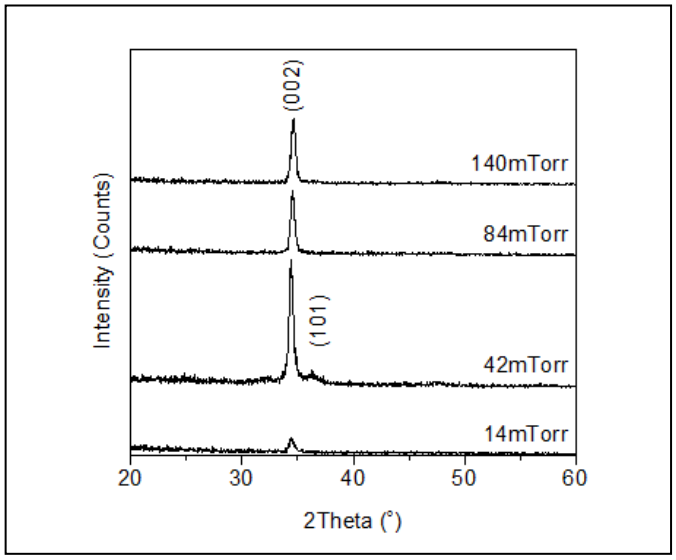

Fig. 4: XRD patterns of ZnO thin films at various background pressures.

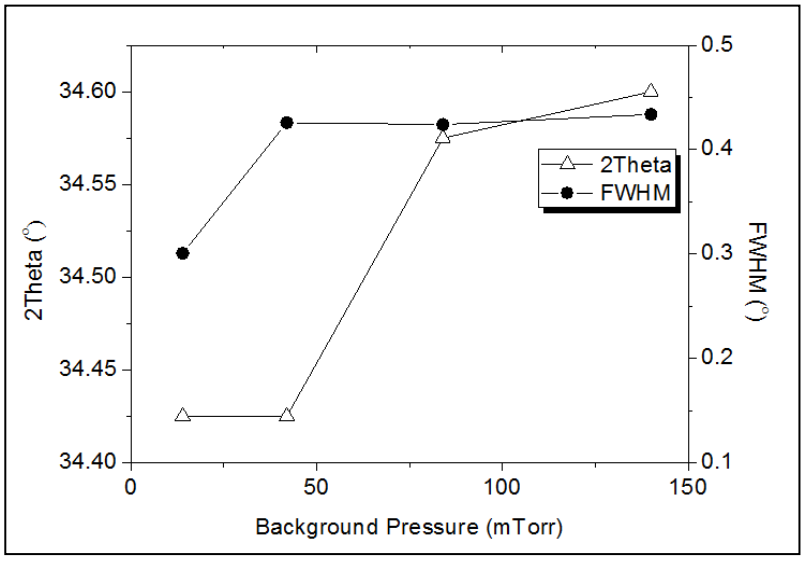

Fig. 5: Position and FWHM of (002) diffraction peak for ZnO thin films at various background pressures.

It can be seen that the position of the (002) peaks of ZnO films, as shown in Fig. 5, increases from 34.425° to 34.6° with the increased in oxygen pressure from 14 mTorr to 140 mTorr. In addition, the values shown are all larger as compared to the bulk ZnO of 34.421°. This indicates that tensile stresses are induced in all films as a result of higher oxygen content that are formed with the increasing background pressure during deposition [13]. As shown in Table 2, an upward trend of oxygen content can be observed from 55.82 at% at 14 mTorr up to 62.06 at% at 84 mTorr.

In Fig. 5, the FWHM of film deposited at 140 mTorr is slightly larger (0.43378°) than the films prepared at lower pressure of 42 mTorr and 84 mTorr (0.42583° and 0.42406°). This implies that its crystallinity is slightly deteriorated, which is consistent with the results from XRD. The degradation of crystallinity at higher oxygen pressure has been suggested due to the prevention of atoms for having sufficient time to search the suitable position in the crystal lattice [13].

The grain size shown in Table 3 decreases steeply from 27.65 nm to 19.53 nm when the oxygen pressure increases from 14 mTorr to 42 mTorr, followed by an insignificant increased in grain size (19.53 nm to 19.62 nm) when the pressure is further increased to 84 mTorr. On the other hand, the surface roughness shows increasing trend from 18.29 nm to 21.76 nm with increasing pressure from 14 mTorr to 140 mTorr. It has been reported that by increasing the level of oxygen, the surface roughness increases, the concentration of oxygen vacancy reduces and grains grow larger [13]. However, significant grain growths with oxygen pressure are not shown in the results.

Table 2: Concentrations of O and Zn (at%) in ZnO thin films at various background pressures

	Background Pressure			
	14mTorr	**42mTorr**	**84mTorr**	**140mTorr**
O [at%]	55.82	56.55	62.06	61.80
Zn [at%]	1.57	2.03	2.34	2.01

Table 3: Properties of ZnO thin films at various background pressures

Background Pressure [mTorr]	**Grain size (XRD) [nm]**	**Surface Roughness RMS [nm]**	**Resistivity, ρ [Ωm]**	**Conductivity, σ [Sm^{-1}]**
14	27.65	18.29	0.8239	1.2137
42	19.53	18.47	0.4598	2.1749
84	19.62	21.52	0.4070	2.4570
140	19.18	21.76	0.7370	1.3569

From Table 3, the resistivity drops dramatically when the oxygen pressure for deposition is increased. The lowest electrical resistivity of 0.407 Ωm is obtained at 84 mTorr, which corresponds to the highest conductivity of 2.457 Sm^{-1}. It is found that higher conductivity is coupled with larger grains and rougher surface, which is similarly elucidated above (in session: substrate temperature effect), where the enhancement in conductivity is due to the reduction in grain boundaries as grains grow larger which in turns decrease the grain boundary scattering [13].

4. Conclusions

The substrate temperature range of RT to 300°C (at fixed oxygen pressure of 14 mTorr) and the oxygen pressure range of 14 mTorr to 140 mTorr (at fixed substrate temperature of 100°C) of pulsed-laser deposited ZnO thin films for TE application were investigated. All the films deposited in these experimental conditions show strong *c*-axis (002) orientation growth. The electrical conductivity can be tailored, where the maximum of 17.4825 S/m and 2.457 S/m were obtained at optimized conditions of 300°C at 14 mTorr and 84 mTorr at 100°C, respectively. The high conductivity values are contributed to the reduction in grain boundaries, and hence, the grain boundary scattering, as a result of larger grains and rougher surfaces that were produced. These morphologies are attributes of the higher energy that aided the particle mobility when substrate temperature is increased, and the lower concentration of oxygen vacancy when more oxygen pressure is supplied, respectively.

Acknowledgements

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