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Cross-plane temperature-dependent thermal conductivity of Al-doped zinc oxide thin films

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ABSTRACT

We measured the cross-plane thermal conductivity of Al-doped zinc oxide (ZnO) with 0.5–1.5 at.% of Al. Al-doped ZnO thin films were prepared on SiO_2/Si substrates by sol–gel spin coating. Thermal conductivity was measured at temperatures ranging from 20 to 300 K, using the four-point-probe 3-ω method. The measured thermal conductivity of the Al-doped ZnO thin films decreased as Al doping increasing up to 1.5 at.%. The average thermal conductivities of un-doped and Al-doped ZnO thin films were 1.1–5.6 W/m · K at 300 K. We suggest that this reduction of thermal conductivity with Al doping could reflect the combined effects of enhanced phonon scattering from grains and Al impurities, and the increasing porosity of the films with increasing Al doping. We also confirmed that the thermal conductivity of the films depends on Al doping.

1. Introduction

Zinc oxide (ZnO) films with wide bad gap (3.3 eV) and the potential for convenient doping have attracted attention for their use in applications such as gas sensors [1], solar cells [2,3], and transparent conducting oxides [4]. Several techniques have been reported, including reactive evaporation [5], radio-frequency (RF) sputtering, direct current (DC) and ion beam sputtering [6,7], chemical vapor deposition [8], spray pyrolysis [9], and sol–gel process [10–16]. Among these techniques, the sol–gel process is one of the simplest and least expensive methods for growing ZnO thin films, especially on large-scale surfaces [17–22].

The efficiency of a thermoelectric (TE) device depends on its material properties expressed through the dimensionless figure of merit ZT, which is defined as $ZT = S^2\sigma T/\kappa$, where $S^2\sigma$ is the power factor, S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the total thermal conductivity. High-performance TE materials with high power factor and low thermal conductivity, resulting in high ZT values, have been documented. It was reported that ZnO doped with aluminum (Al) impurity is a promising high-ZT material for power energy harvesting from heat, owing to its high melting point, high σ, and high S [23]. In addition, this material is advantages for high-temperature TE applications because of its excellent TE properties as well as thermal stability and excellent oxidation resistance [24]. Nevertheless, previous reports investigating Al-doped ZnO thin films were focused on phenomena such as transparency and conductivity [25], thin film transistor (TFT) effect [26], the doping effect and the annealing temperature of the films [27,28], as well as on theoretical investigations of electronic structure and TE materials [29]. In 2014, Loureiro et al. reported transparent Al-doped ZnO thin films with enhanced TE properties prepared by using RF and pulsed DC magnetron sputtering [30]. These authors reported ZT value at least threefold higher than the value of ~0.1 reported previously for Al-doped ZnO thin films. Therefore, these high-TE properties of ZnO thin films can be very useful and noteworthy for enhancing the TE properties for future cooling and power-generation device applications. However, only few reports addressed the effect of doping, porosity, and grain size on thermal transport properties of ZnO thin films, such as thermal conductivity, for temperatures ranging from 20 to 300 K. In addition, there are no theoretical studies on thermal conductivity of Al-doped ZnO thin films.

In this study, we investigated the effect of Al doping on the temperature-dependent thermal conductivity of ZnO thin films (thickness of 150 nm) for temperatures ranging from 20 to 300 K, using the 3-ω method. Al-doped ZnO thin films were prepared on SiO_2/Si substrates by sol–gel spin coating. We also investigated the effects of porosity and grain size, which was controlled by the Al concentration in ZnO films. We then theoretically analyzed film thermal conductivity employing the Sondheimer's model.

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2. Experimental details

2.1. Sample preparation

150-nm-thick ZnO thin films were prepared by sol–gel spin coating method. $AlCl_3{\cdot}6H_2O$ and $Zn(CH_3COO)_2{\cdot}2H_2O$ were used for growing Al-doped ZnO thin films as a starting material. A detailed description of the sol–gel process can be found elsewhere [4,31]. In brief, for investigating the effect of Al dopant concentration on the thermoelectric property of ZnO thin films, the Al concentration was varied from 0 (un-doped), through 0.5, and to 1.5 at.% with respect to Zn. The mixture solutions were then stirred at 60 °C for 2 h to obtain homogeneous solutions. Un-doped and Al-doped (0.5 and 1.5 at.%) ZnO thin films were deposited on SiO_2 (300-nm-thick)/Si substrates by sol–gel spinning coating with spin coating at 3000 rpm for 20 s at room temperature. The coated thin films were then annealed at 650 °C for 1.5 h. The crystal structure and the surface morphology of the thin film were characterized using X-ray diffraction (XRD, Rigaku O/MAX-RC) and field emission scanning electron microscope (FE-SEM, SIGMA/Carl Zeiss) equipped with energy dispersive X-ray spectrometry (EDX). The out-of-plane (cross) thermal conductivity (κ) of the thin films was measured using four-point-probe 3-ω technique based on the application of an alternating current (AC) with angular frequency, which was first developed by Cahill in 1990 [32]. A detailed description of the measurement set-up was given elsewhere [33,34]. For the thermal conductivity measurements, a narrow metallic strip (Ti/Au = 10/300 nm) consisting of four-point probe electrodes was first patterned onto the sample using conventional photolithography. The patterned four-point-probe electrodes can act as both a heater and a sensor for measuring the thermal conductivity of thin films [34]. Thermal transport measurements were performed in the temperature range of 20–300 K in closed cycle refrigerator (Janis, USA) system equipped with turbo pump (Edward, UK), where the measurement system was electrically shielded to prevent heat loss due to convection and radiation. In addition, to minimize the vibrational noise from the ground, the measurements were performed on an isolated optical table.

2.2. Thermal conductivity measurement

Schematic of the experimental setup and circuit connections of the 3-ω system for thermal conductivity measurement is shown in Fig. 1(a). The source meter (Keithley 6221, USA) was connected to both metallic pads for AC current (I_0) as shown in Fig. 1(a). The current I_0 with an angular modulation frequency 1-ω was applied to generate Joule heat and temperature fluctuations at a frequency of 2-ω. The resistance of the narrow metallic strip is proportional to the temperature that leads to a voltage fluctuation of 3-ω across the sample. A lock-in amplifier (A-B mode, SR-850, Stanford Research System, USA) connected to the two metallic pads in the middle measured the 3-ω voltage fluctuation along the narrow metallic strip. In the differential 3-ω method, the total temperature oscillation, $\Delta T(\omega)$, for a multilayer sample is [35]

$$\Delta T(\omega) = \frac{P}{\pi\kappa_s}\left\{\frac{1}{2}\ln\left(\frac{D_s}{b^2}\right) + 0.923 - \frac{1}{2}\ln(2\omega) - \frac{i\omega}{4}\right\} + \frac{Pd_f}{2b\kappa_f} \quad (1)$$

where P is the supplied power-per-unit-length of the narrow metallic line; D_s is the thermal diffusivity; d_f is the thin film thickness; b is the width; and κ_s and κ_f are the thermal conductivities of the SiO_2(300-nm-thick)/Si substrate and 150-nm-thick ZnO thin film, respectively. $\Delta T(\omega)$ is obtained from measurements of the third-harmonic root-mean-square voltage drop, $V_{rms\text{-}3\omega}$, across the metallic line, using the following equation:

$$\Delta T(\omega) = \frac{2V_{rms\text{-}3\omega}}{\alpha I_0 R_0},\quad \alpha = \frac{1}{R_0}\left(\frac{dR_0}{dT}\right) \quad (2)$$

where α is the temperature coefficient of the resistance R_0 of the Ti/Au metallic strip. Finally, κ_f is determined from Eq. (3), which can be derived from the second term in Eq. (1), as follows:

$$\kappa_f = \frac{Pd_f}{2b\{\Delta T_{s+f}(\omega) - \Delta T_s(\omega)\}} \quad (3)$$

where $\Delta T_{s+f}(\omega)$ is the temperature oscillation of the in-phase component for a SiO_2/Si substrate with thin film and $\Delta T_s(\omega)$ is the temperature oscillation of the in-phase component without the thin film. Thus, the cross-plane thermal conductivity of thin films can in general be evaluated from Equation (3), provided $\Delta T_{s+f}(\omega)$ and $\Delta T_s(\omega)$ are measured separately using the 3-ω method in the 20–300 K temperature range. Fig. 1(b) shows the temperature oscillation of the in-phase component, $\Delta T_{s+f}(\omega)$, for the 0.5 and 1.5 at.% Al-doped ZnO thin films with un-doped ZnO thin film, where the $\Delta T_s(\omega)$ value of the substrates (SiO_2/Si) is also included for the reference. From Fig. 1(b), we evaluated the thermal conductivity for the SiO_2 (300-nm-thick)/Si substrate as ~1.25 W/m K at 300 K, which agrees well previously reported result [35].

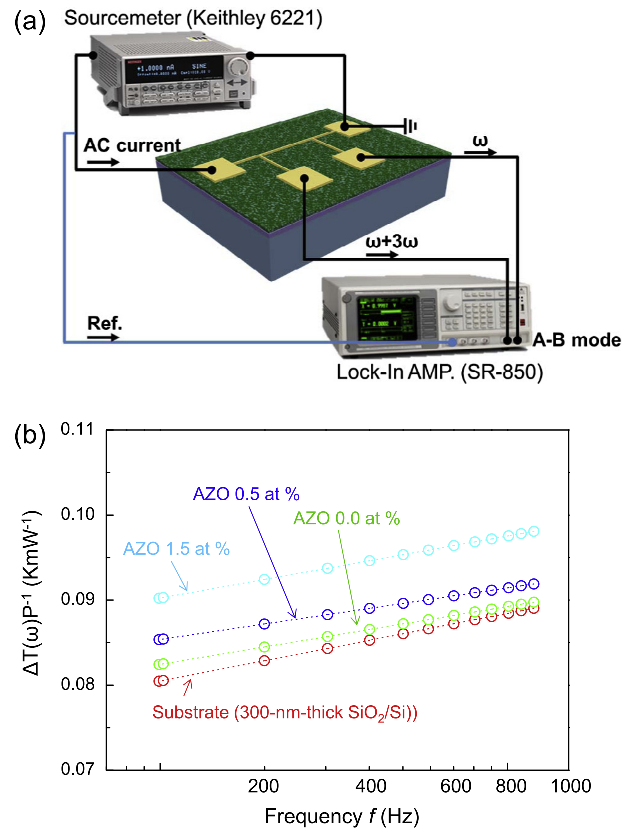

Fig. 1. (a) Schematic of the four-point-probe 3-ω method for thermal conductivity measurement of Al-doped ZnO thin films. (b) Temperature oscillation in ZnO thin films with 0, 0.5, and 1.5 at.% Al concentration as a function of the applied frequency. In this figure, temperature oscillation for a SiO_2 (300-nm-thick)/Si substrate is also included for calculating the differential thermal conductivity.

3. Results and discussion

3.1. Material characteristics of Al-doped ZnO thin film

In this study, we evaluated grain sizes, detailed material properties, and thermal transport characteristics of Al-doped ZnO thin films by performing measurements using SEM, XRD, and cross-plane 3-ω technique. Fig. 2(a)–(i) shows the SEM images of un-doped ZnO thin films and Al-doped ZnO thin films that were prepared on the SiO_2/Si substrates at 300 K. In all film images shown in this figure, the grains are clearly visible and are uniformly distributed over the films surface. Introducing the Al dopant into the un-doped ZnO thin films reduced the grain size as shown in Fig. 2. This suggests that Al dopant obstructs grain growth, as shown in Fig. 2. Fig. 2 also shows the cross-sectional images of un-doped (Fig. 2(c)) and Al-doped (Fig. 2(f) and (i)) ZnO thin films on SiO_2/Si structures, demonstrating that the ZnO thin films were successfully grown on the substrates. Fig. 3(a) shows the XRD patterns of un-doped (0 at.%) and Al-doped (0.5 and 1.5 at.%) ZnO thin films prepared on the Si substrates. As shown in figure, (002) peaks of un-doped and Al-doped ZnO thin films increased following the introduction of Al dopants. The (002) peaks increased ~1.5 and 3 times in the Al-doped ZnO thin films after introducing the Al dopant 0.5 and 1.5 at.%, respectively. This implies that the crystallinity had improved after introducing the Al dopant into ZnO thin films. Full width at half maxima (FWHM) of (002) were extracted from the XRD 2θ values (Fig. 3(b)). The FWHM increased as increasing amount of Al dopant (Fig. 3(b)). This suggests that the concentration of (002) crystallites with different orientation increased as well. In addition, the