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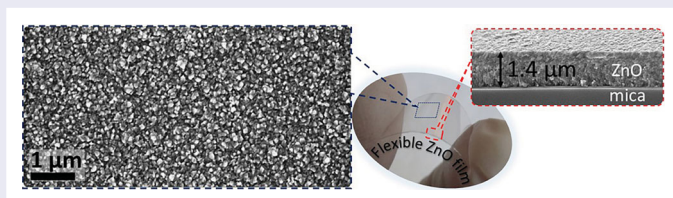
Donor-doped ZnO thin films on mica for fully-inorganic flexible thermoelectrics

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ABSTRACT

The development of fully-inorganic thin flexible materials is important for flexible thermoelectric applications in a wide temperature range, such as harvesting power from hot curved surfaces (e.g. hot pipes). Here, we investigate the thermoelectric properties of a series of ZnO:Ga,Al thin films with varying dopant concentration deposited on flexible mica substrate by atmospheric pressure metal-organic chemical vapor deposition. The films are bendable, while sustaining the high power factor, above $1 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-2}$ for singly doped Zn_{0.99}Ga_{0.01}O film in a wide temperature range, from room temperature to 400°C.



IMPACT STATEMENT

For the first time we demonstrate here that ZnO-film-on-mica can be a promising n-type candidate for fully-inorganic flexible thermoelectrics, especially, for applications at elevated temperatures

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KEYWORDS

Thermoelectric; ZnO; thin film; fully-inorganic; flexible

1. Introduction

With the emergence of flexible electronics, conducting oxides have attracted attention [1–3] because their constituent raw materials are nontoxic, abundant and low-cost. In contrast, for thermoelectric applications, oxide materials are conventionally considered to be suitable for high-temperature ranges, where the active materials are subjected to a large temperature gradient (ΔT), say couple of hundred degrees Celsius. For applications near room temperature up to a few hundred degrees, they have received less attention because of the low-temperature value of thermoelectric figure of merit ZT ($= S^2 T / \rho \kappa$, where S , ρ , κ , and T are the Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively) of conventional oxide materials. However, our recent investigations [4–6] show that fully-inorganic *p*-type Ca₃Co₄O₉ thin films can retain a high power factor (S^2 / ρ) near room temperature and thus be useful both for near-room-temperature flexible thermoelectrics, e.g. wearable applications (harvesting electrical

power from body heat) and at higher temperature for harvesting heat from hot curved surface (e.g. hot pipes) for power generation. For high output power, achieving high power factor is more important than high ZT [7].

There have been extensive investigations in the area of flexible thermoelectrics based on organic [8–12] and organic–inorganic hybrid materials [13–16]. The drawback of organic materials is that they cannot sustain high temperature, typically above 200°C, and easily degrade over time [17,18]. For applications at somewhat elevated temperatures (e.g. harvesting power from hot pipes), fully inorganic flexible films would be required [16]. Despite the recent success in the growth of fully-inorganic flexible *p*-type thin films [4,5,19] the progress in *n*-type oxide materials for fully-inorganic flexible thermoelectric applications is still elusive. Zinc oxide (ZnO) is a wide band gap semiconductor, which is well known as *n*-type material for transparent conducting coatings, upon doping by Al, Ga, In, etc. [20]. A high power factor of $20 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-2}$ near room temperature is reported for

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bulk ZnO [21]. Thus, thin films of ZnO can be promising as *n*-type counterpart for fully-inorganic flexible thermoelectric applications, if they can be made mechanically flexible and the high power factor is retained.

Here, we investigate a series of single- and dual-doped ZnO:Al,Ga thin films grown on flexible and high-temperature stable muscovite mica substrates. Muscovite mica a layered structure, where aluminosilicate layers of muscovite mica are weakly bonded by van der Waals forces, leading to the easy cleavage along the {001} planes. Due to this weak interlayer bonding, muscovite mica is easily bendable and allow flexible applications [22,23].

2. Experimental section

ZnO films were deposited by atmospheric pressure metalorganic chemical vapor deposition (APMOCVD) using Zn acetylacetonate (ZnAA) as a solid-state single source precursor. Doping was realized by adding a corresponding amount of Ga(AA) and Al(AA) to the precursors mixture. Growth was performed at a substrate temperature of 550°C and Ar buffer gas flow rate 50 sccm, which was earlier reported as optimal conditions for the growth of high-quality ZnO films [24]. Four samples, namely $\text{Zn}_{0.99}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.96}\text{Al}_{0.03}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.96}\text{Al}_{0.02}\text{Ga}_{0.02}\text{O}$, were prepared following the films growth procedure described elsewhere [24,25].

The crystal structure and morphology of the films were characterized by $\theta - 2\theta$ X-ray diffraction (XRD) analyses using monochromatic Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), and scanning electron microscopy (SEM, LEO 1550 Gemini). $\theta - 2\theta$ XRD scans were performed with a Philips PW 1820 diffractometer. The composition of the films was determined by EDS in SEM, with an accuracy $\pm 5\%$. The temperature-dependent in-plane electrical resistivity and Seebeck coefficient were simultaneously measured using an ULVAC-RIKO ZEM3 system.

3. Results and discussion

Figure 1(a) shows optical images of the films $\text{Zn}_{0.99}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.96}\text{Al}_{0.03}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.96}\text{Al}_{0.02}\text{Ga}_{0.02}\text{O}$. The transparency of the films visibly varies for different films with varying Al and Ga-content. The films are bendable as due to the flexible nature of the mica substrate, but with no deterioration of thermoelectric performance of the films. Figure 2(b) shows the bended $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$ film of thickness $1.4 \mu\text{m}$ with mica substrate of thickness $60 \mu\text{m}$, showing its mechanical flexibility. The film is bendable to the bending radius of 14 mm without developing cracks in the film, as confirmed by an optical microscope.

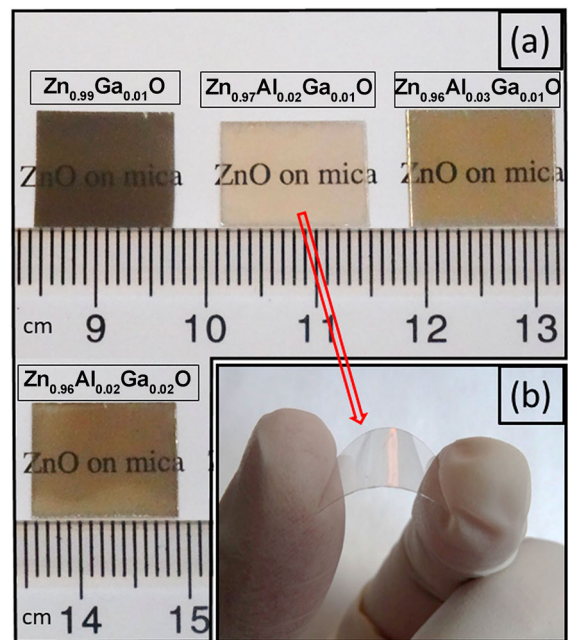


Figure 1. (a) Optical images of the films $\text{Zn}_{0.99}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.96}\text{Al}_{0.03}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.96}\text{Al}_{0.02}\text{Ga}_{0.02}\text{O}$, and (b) bended $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$ film.

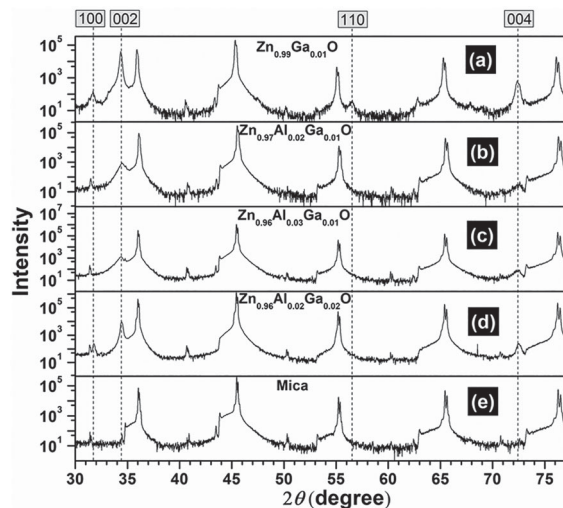


Figure 2. $\theta - 2\theta$ XRD patterns of the films (a) $\text{Zn}_{0.99}\text{Ga}_{0.01}\text{O}$, (b) $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$, (c) $\text{Zn}_{0.96}\text{Al}_{0.03}\text{Ga}_{0.01}\text{O}$, (d) $\text{Zn}_{0.96}\text{Al}_{0.02}\text{Ga}_{0.02}\text{O}$, and (e) bare mica substrate.

Figure 2 shows $\theta - 2\theta$ XRD patterns of a bare mica substrate and the films $\text{Zn}_{0.99}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.96}\text{Al}_{0.03}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.96}\text{Al}_{0.02}\text{Ga}_{0.02}\text{O}$. XRD peaks at 2θ angles 23.68° , 34.45° , 56.52° , 62.79° , 72.40° are reflections from (100), (002), (110), (004) planes of ZnO, respectively. The films were found to be polycrystalline, however, with preferential orientation along [0001] directions. The presence of a secondary (100) orientation in the films $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.96}\text{Al}_{0.03}\text{Ga}_{0.01}\text{O}$ is evident, as seen by the presence of a (100) peak in the θ - 2θ XRD patterns. The 002 peaks of the films

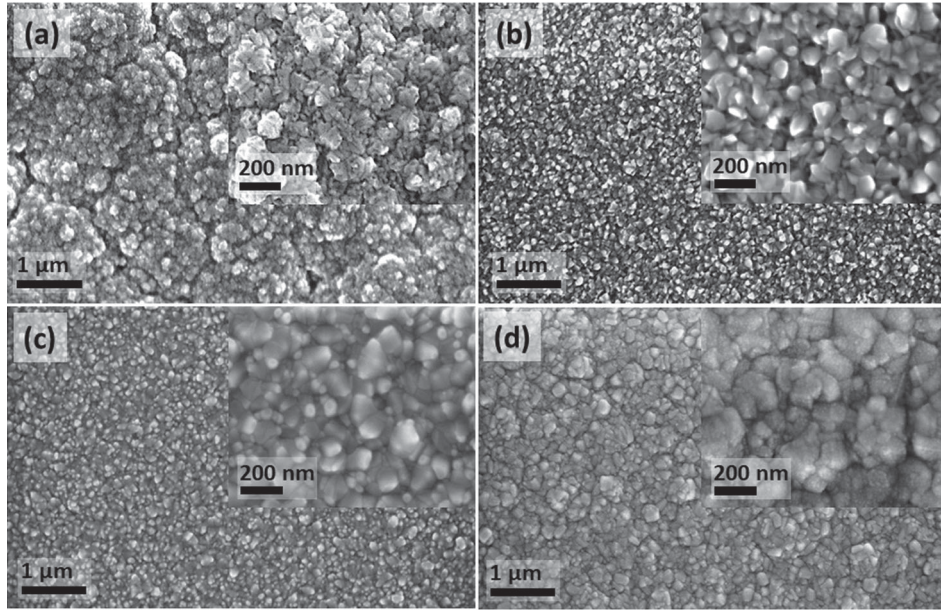


Figure 3. SEM images of the films (a) $\text{Zn}_{0.99}\text{Ga}_{0.01}\text{O}$, (b) $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$, (c) $\text{Zn}_{0.96}\text{Al}_{0.03}\text{Ga}_{0.01}\text{O}$, (d) $\text{Zn}_{0.96}\text{Al}_{0.02}\text{Ga}_{0.02}\text{O}$.

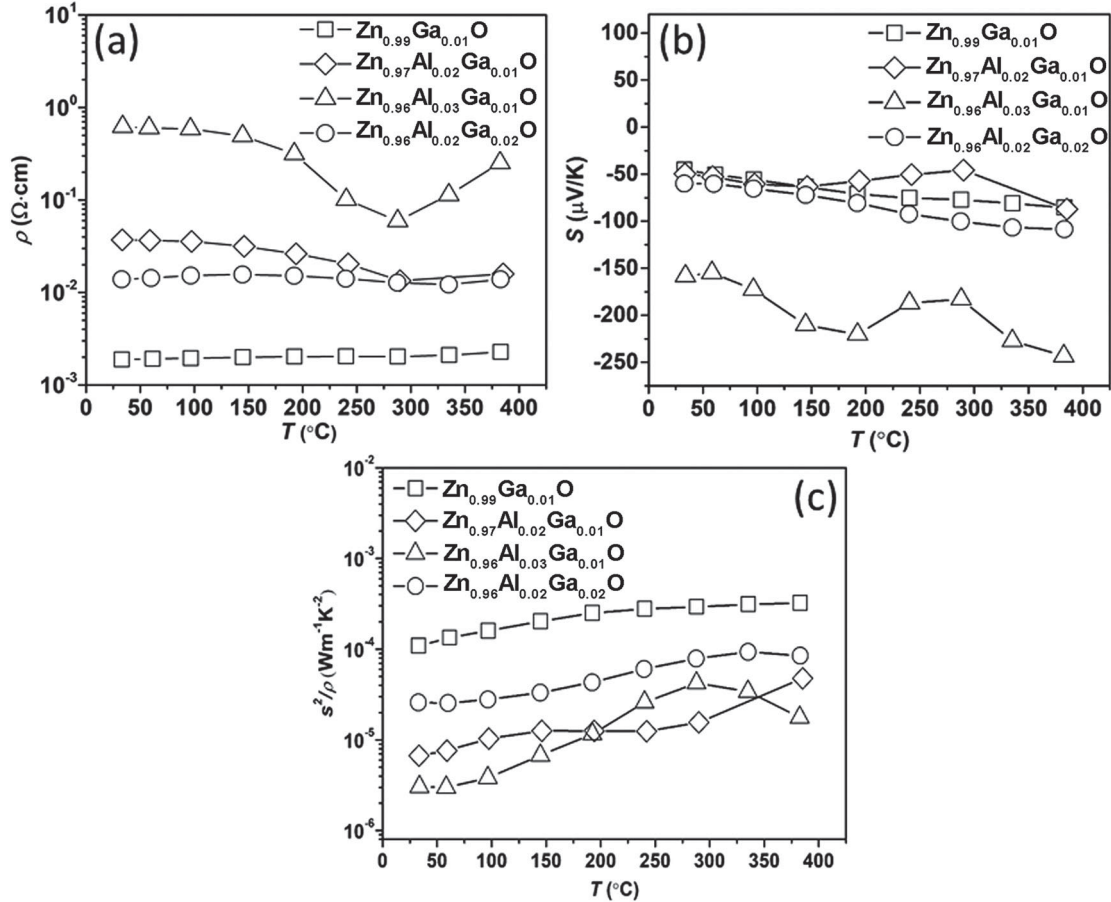


Figure 4. Temperature-dependent (a) electrical resistivity, (b) Seebeck coefficient, and (c) power factor of all films from room temperature to 400°C.

$\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$ and $\text{Zn}_{0.96}\text{Al}_{0.03}\text{Ga}_{0.01}\text{O}$ are relatively broader than the other films, which is attributed to the reduced grain size of the films.

This microstructure is a result of a self-textured competitive growth of polycrystalline material [26]. The nucleation results in initial growth of grains with different

orientation, forming the first layers of the film. Later, the grains which have their (002) plane up—the lowest surface energy crystal plane—are growing faster, thus occupying the volume and forming the c-axis textured film, with c-axis perpendicular to the substrate plane. Figure 3(a–d) shows the top-view SEM images of the films $\text{Zn}_{0.99}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.96}\text{Al}_{0.03}\text{Ga}_{0.01}\text{O}$, $\text{Zn}_{0.96}\text{Al}_{0.02}\text{Ga}_{0.02}\text{O}$, respectively. The insets of the figures show magnified images of small portions of the respective films. Varying surface morphology of the films is apparent from Figure 3.

Figure 4(a) shows the temperature-dependent electrical resistivity of the deposited films. The electrical resistivity of the film $\text{Zn}_{0.99}\text{Ga}_{0.01}\text{O}$ is the lowest throughout the temperature range measured. Earlier, we have reported that 1 wt.% of Ga precursor results in the lowest resistivity of ZnO films [25]. This can be explained as due to efficient providing of donors upon Ga substitution of Zn in the crystal lattice. Further increase of Ga content results in increased resistivity, which is apparently due to incorporation of Ga atoms as interstitials.

The electrical resistivity increases in $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$ due to the additional incorporation of Al to $\text{Zn}_{0.99}\text{Ga}_{0.01}\text{O}$, with subsequent change from Zn:Ga system to Zn:Al,Ga system. With further increase in Al-content of the film $\text{Zn}_{0.96}\text{Al}_{0.03}\text{Ga}_{0.01}\text{O}$ its electrical resistivity increased to the highest value throughout the temperature range measured. This increase in electrical resistivity is consistent with the observation reported elsewhere [27], and may be related to the formation of Al-rich secondary phases acting as scattering center for charge carriers. With the increase in Ga-doping in $\text{Zn}_{0.96}\text{Al}_{0.02}\text{Ga}_{0.02}\text{O}$ the electrical resistivity is slightly decreased as compared to $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$. This indicates that Ga goes to lattice site, contributing additional electrons to take part in transport process.

Figure 4(b) shows the temperature-dependent Seebeck coefficient of all the films. The film $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$ exhibits the highest absolute value of the (negative) Seebeck coefficient throughout the temperature range measured. The Seebeck coefficient of all the films varies with temperature following a similar trend as electrical resistivity.

Figure 4(c) shows the temperature dependent power factor of the films. The film $\text{Zn}_{0.99}\text{Ga}_{0.01}\text{O}$ exhibits the highest power factor, above $1 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-2}$, throughout the temperature range measured. Although the room temperature value of the power factor of the film $\text{Zn}_{0.99}\text{Ga}_{0.01}\text{O}$ is somewhat lower than the value for ZnO thin films on rigid Si substrates reported by Lee et al. [28], it is comparable to the value reported elsewhere

[29,30,31], and can be suitable as *n*-type counterpart to flexible *p*-type $\text{Ca}_3\text{Co}_4\text{O}_9$ films [4,5].

To examine the effect of bending stress on thermoelectric performance the flexible film $\text{Zn}_{0.97}\text{Al}_{0.02}\text{Ga}_{0.01}\text{O}$ was subjected to 100 times bending and Seebeck measurement was performed. No notable change in Seebeck coefficient and electrical resistivity is observed. The small variation in the values is found to be well below the error limit specified by the ULVAC-RIKO ZEM3 system.

4. Conclusions

Thermoelectric properties of a series of ZnO-films on flexible mica substrates with varying dopant concentration, grown by APMOCVD method, have been investigated. Dual doping by Al and Ga at Zn-site is found to increase the electrical resistivity of the films, yielding reduced power factor throughout the temperature range measured. The singly doped $\text{Zn}_{0.99}\text{Ga}_{0.01}\text{O}$ film is found to exhibit the lowest electrical resistivity, yielding the highest power factor with room temperature value $\sim 1 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-2}$. With this high power factor the singly doped ZnO:Ga film is a promising *n*-type candidate for fully-inorganic flexible thermoelectric applications in a wide temperature range.

Disclosure statement

No potential conflict of interest was reported by the authors.

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