

REVIEW

Effect of dopants and nanostructuring on the thermoelectric properties of ZnO materials

To cite this article: Son D N Luu et al 2019 Adv. Nat. Sci: Nanosci. Nanotechnol. 10 023001

View the article online for updates and enhancements.

Adv. Nat. Sci.: Nanosci. Nanotechnol. 10 (2019) 023001 (14pp)

Review

Effect of dopants and nanostructuring on the thermoelectric properties of ZnO materials

Son D N Luu^{1,2}, Tuan Anh Duong^{3,4} and Thang Bach Phan^{1,5}

¹Center for Innovative Materials and Architectures (INOMAR), Vietnam National University, Ho Chi Minh City 721337, Vietnam

² The Institute of Advanced Manufacturing Technology, Centre of Thermoelectric Materials Research, 37 A Wroclawska, 30-011 Cracow, Poland

³ Phenikaa Institute for Advanced Study and Faculty of Materials Science and Engineering, Phenikaa University, Yen Nghia, Ha-Dong District, Hanoi 10000, Vietnam

⁴ Phenikaa Research and Technology Institute, A&A Green Phoenix Group, 167 Hoang Ngan, Hanoi 10000, Vietnam

⁵Laboratory of Advanced Materials, University of Science, Vietnam National University, Ho Chi Minh City, Vietnam

E-mail: pbthang@inomar.edu.vn

Received 17 April 2019 Accepted for publication 7 May 2019 Published 30 May 2019



Abstract

Zinc oxides have attracted attention in high-temperature waste heat recovery due to their high melting points. This review aims to provide a comprehensive summary of the effects of dopant on thermoelectric properties of ZnO based bulk, thin films, nanowire as well as the effects of nanostructuring on ZnO based materials. In general, the thermoelectric performance can be enhanced by a single doping. Among single dopant elements, Al dopant seems to be effective dopant resulting in better thermoelectric properties. However, the solubility limit of the dopant in single doping limits the improvement of thermoelectric performance. Efforts in dual doping to improve the thermoelectric properties of ZnO materials have been conducted. As a result, the drastic improvement of the thermoelectric performance from Al-Ga dually doped ZnO bulk and Ga-In dually doped ZnO thin films shows strong evidence of this approach. In addition to doping effects, the thermoelectric performance can also be enhanced through structural effects such as mismatches between the film and substrate, morphology, thermal treatments or introducing nano-precipitated materials. In addition, the low-dimensional structure such as nanowire structure is promising for improving the thermoelectric properties of materials because of their strong quantum confinement effect. This leads to the increase of the Seebeck coefficient according to the Mott's relationship without lowering the electrical conductivity.

Keywords: ZnO thermoelectric materials, single and dual doping, thermal conductivity, nanostructuring

1. Introduction

Thermoelectric (TE) power has been recently discussed as an alternative renewable and green energy. Indeed, the thermoelectric generator, without moving parts, enables direct conversion of heat into electricity driven by thermoelectric effects. Heat, produced by automobiles, industrial facilities, power plants, and even through home heating, is discarded into the atmosphere or water as waste. Also, more than 60%of the primary energy in fossil fuels is released as waste heat. Therefore, thermoelectric power, particularly TE materials have drawn much attention. The efficiency of thermoelectric materials is presented by the dimensionless figure of merit (*ZT*) which is derived from a combination of three physical parameters: Seebeck coefficient (S), electrical conductivity (σ) and thermal conductivity (κ): $ZT = (S^2 \sigma / \kappa)T$, with the absolute temperature T. A good thermoelectric material would ideally possess both high electrical conductivity (like a metal) and Seebeck coefficient (like a semiconductor) while the thermal conductivity is low (like an insulator). This results in the maximum temperature difference, which generates a high output voltage per unit temperature gradient [1]. However, the physical relationship of these three parameters makes it challenging because the Wiedemann–Franz law shows that κ is proportional to σ and the simultaneous enlargement of S and σ is limited by the Pisarenko relationship [2]. It means that improvement in σ not only increases the thermal conductivity κ but also decreases the Seebeck coefficient S, leading to a difficult improvement in the power factor $PF = \sigma S^2$ and ZT, simultaneously. Several approaches to enhance ZT have been reported, including band structure engineering by doping or changing composition to increase the electrical conductivity of materials [3] or band alignment to maintain hole mobility [4]. On the other hand, the thermal conductivity can be reduced by nanostructure engineering, introducing structural defects such as point defects, dislocations, and interfaces to enhance phonon scattering or grain boundary scattering [5–9].

Thermoelectric metal oxides are attractive for hightemperature applications due to their high chemical stability and low raw material costs. However, metal oxides are ionic compounds which consist of metal cations and oxygen anions alternately linked by Coulombic force. It is well known that the metal-oxygen bonds are largely polarized, so conducting electrons localize around the cations. In addition, carrier mobilities of metal oxides are generally 2-3 orders lower than those of covalent compounds due to the smaller overlapping of atomic orbitals between the atoms. Moreover, a high lattice thermal conductivity is induced due to large bonding energies of the ionic bonds. Thus, metal oxide materials have low ZT value. However, metal oxide materials, which are highly durable at high temperature in air, non-toxic, low cost and show minimal environmental impact, are still under investigation for thermoelectric applications [5].

ZnO materials have drawn vast attention in the past decades due to their interesting characteristics: non-toxic, abundant resource, cheap and very stable at high temperature (up to 1000 °C). Many researchers have been focusing on studying ZnO for thermoelectric applications to improve electrical conductivity and decrease thermal conductivity [5–9]. Due to the solubility limit of the single dopant, simultaneous control of electrical conductivity, Seebeck coefficient and thermal conductivity for a high ZT reach threshold. Therefore, many research groups have been investigating the effects of dual doping on the thermoelectric properties of ZnO.

In addition, it is well known that the low-dimensional structure is promising for improving the thermoelectric properties of materials because of their strong quantum confinement effect. Therefore, in this review, we will provide a comprehensive summary of the effect of dopants and



Figure 1. (a) A STEM micrograph of the Al-doped ZnO nanocomposites and EDS line profile of Zn, O, and Al. (b), (c), and (d) are the corresponding EDS elemental mapping results of Zn, O, and Al, respectively. $ZnAl_2O_4$ nanoprecipitates are marked by yellow circles in (d). (e) A HRTEM micrograph of a $ZnAl_2O_4$ nanoprecipitate and the corresponding FFT image (inset). [Reprinted with permission from [18]. Copyright 2012 Royal Society of Chemistry].

nanostructuring on the thermoelectric performance of ZnO materials.

2. Overview of the thermoelectric properties of pure zinc oxide

ZnO is an *n*-type semiconductor with a wide direct band gap of ~ 3.2–3.5 eV [10] and a large free-exciton binding energy [11–14] so that excitonic emission processes can persist at or even above room temperature [7, 15]. ZnO has three different crystal structures: the wurtzite, rock salt, and zincblende structures. However, at the ambient conditions, the most common and stable phase is the wurtzite. In this paper, we focus on discussing the thermoelectric properties of ZnO with the wurtzite structure. The wurtzite structure has a hexagonal unit cell with a ratio of $c/a \sim 1.633$ and belongs to the space group of C_{6v}^4 or $P6_{3mc}$. The structure composes two hexagonal-close-packed (hcp) sublattices in which the O^{2-} and Zn²⁺ ions are covalently bonded. In the sublattice, each Zn²⁺ is coordinated by four O^{2-} at the edges of a tetrahedron [10].



Figure 2. Schematics of the consolidation process for (a) rods, (b) platelets and (c) nanoparticles, respectively. The consolidated samples of the rods and platelets were cut and characterized along both perpendicular (tp) and parallel (kp) directions to the pressure axis. The anisotropy of the consolidated sample of the nanoparticles was negligible. [Reprinted with permission from [20]. Copyright 2014 Royal Society of Chemistry].

In this structure, ZnO possesses high electron mobility and thermal conductivity due to the sp^3 hybrid valence electrons in its wurtzite lattice structure [10]. Lin *et al* [16] reported very high electron mobility (~200 cm²V⁻¹s⁻¹) of single crystal ZnO at room temperature, fascinating the interests of its electrical properties. However, the biggest drawback of this material for TE applications is its high thermal conductivity. At 300 K, the thermal conductivity of pure ZnO is around 49 Wm⁻¹K⁻¹ and decreases to a value of 10 Wm⁻¹K⁻¹ at 1000 K [17]. Therefore, to improve the thermoelectric performance of pure ZnO, apart from improving electrical conductivity, most efforts focus on reducing the thermal conductivity.

3. Single-dopant doped ZnO based bulks and thin films

The thermoelectric performance of ZnO materials has been upgraded with single dopant doping, such as Al [17–23], Bi [24], In [25–28], Fe [29], Ni [30, 31], Sb [32], Sn [33], Dy [34], and Ga [35, 36]. It is noted that dopants with heavier atomic mass compared to the Zn atom are preferred due to its contribution to decreasing the lattice thermal conductivity by introducing more mass fluctuations. In addition, the smaller ionic radius of the dopant also induces smaller distortion of the host crystal structure.

Ohtaki *et al* showed that Al dopant could improve the thermoelectric properties of ZnO with a significantly increased ZT [12, 17]. The carrier concentration of ZnO is



Measurement Temp. (K)

Figure 3. Temperature dependence of figure-of-merit, *ZT*, of the samples. [Reprinted with permission from [20]. Copyright 2014 Royal Society of Chemistry].

increased from $5.2 \times 10^{17} \text{ cm}^{-3}$ of pure ZnO to $7.2 \times 10^{19} \text{ cm}^{-3}$ of 2 at% Al-doped ZnO. It results in a ZT value of 0.3 at 1273 K in which the thermal conductivity κ is about 7 Wm⁻¹K⁻¹, and the combined power factor *PF* is $1.4 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-1}$ at 1273 K.

Due to the limited solubility of dopant in ZnO, high dopant concentration can lead to the secondary phase precipitated in the ZnO matrix, which also contributes to κ reduction. Nam *et al* [18] reported that ZnAl₂O₄ nanoprecipitates exist in 2 mol% Al-doped ZnO nanocomposite, as shown in figure 1. A drastic reduction in thermal conductivity ($\kappa < 2 \text{ Wm}^{-1}\text{K}^{-1}$) was achieved in the nanocomposite, and the maximum *ZT* of 0.34 was obtained at 1073 K [18].

In the same manner, Zhao *et al* [19] reported a low thermal conductivity of Al-doped ZnO bulk. The microstructure consisted of a two-dimensional layered network of oriented grains, which interconnect in the third dimension through inter-planar contacts, and grains are embedded with nano-precipitates. Compared with traditional dense ZnO without two-dimensional layered networks, Al-doped ZnO with layered microstructures exhibits a 52% decrease in thermal conductivity [19].

Li *et al* [20] reported the correlation between the morphologies and the thermoelectric properties of Al-doped ZnO bulk material, as shown in figures 2 and 3. The measured ZT values for the samples consolidated from rods and platelets were reported to be 0.16 and 0.25 at 1223 K, respectively. It is noted that the sample consolidated from nanoparticles had fine grains of several hundred nanometers in size and highly distributed nanoprecipitates with sizes from 10 to 15 nm within the ZnO grain interiors or along the grain boundaries, resulting in a ZT value of 0.3 at 1223 K due to the lowered thermal conductivity resulting from scattering at the grain boundaries and nanoprecipitates [20].

Zhang *et al* [21] reported a unique micro/nanostructure was successfully obtained in $Zn_{1-x}Al_xO$ (x = 0, 0.02, 0.03, 0.04 mol) bulks. The nanograins were found to be aligned along the axial direction of the micro-spheres. The

nanostructured bulks $Zn_{0.98}Al_{0.02}O$ bulk achieved a low κ value of 2.1 Wm⁻¹K⁻¹ due to effective scattering occurring at the boundaries and interfaces, resulting in a high ZT value of 0.36 at 1073 K [21].

In the case of heavy ion doping (such as In, Bi) as shown in figure 4, Jood *et al* [24] demonstrated that doping ZnO with In element can significantly enhance ZT. Indium doping leads to low $\kappa \sim 3 \text{ Wm}^{-1}\text{K}^{-1}$ and a high power factor ($PF \sim 1.230 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-1}$), yielding $ZT \sim 0.45$ at 1000 K which is ~80% higher than non-nanostructured In– Zn–O alloys. Although Bi doping also yields a high Seebeck coefficient of $\alpha \sim 500 \ \mu\text{VK}^{-1}$ at 300 K, Bi segregation, grain growth, and defect complexing are unfavorable to increase ZT [24].

Recently, Anju *et al* [34] reported that a ZT of 0.11 at 923 K was achieved for the 0.1 at % of rare earth Dysprosium-substituted ZnO. The enhancements in the TE properties were mainly through the increase in the carrier concentration and the energy filtering of the carriers at the potential barrier formed in the lattice by Dy doping, which has a large atomic size and localized magnetic moment due to the presence of unpaired electrons [34].

In the case of ZnO based thin films, as shown in figure 5, Park *et al* [22] confirmed that the thermal conductivity of ZnO films depends on Al doping. 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 increased Al doping [22].

Besides the effects of metal dopant, non-metal elements also affect the thermoelectric performance. Liu *et al* [23] recently reported the effect of oxygen defects on the thermoelectric properties of Al-doped ZnO films ($Zn_{0.94}Al_{0.06}O_x$). The $Zn_{0.94}Al_{0.06}O_x$ films were deposited at various oxygen pressures (0.1 MPa and 0.12 MPa). The conductivity and Seebeck coefficient were reported to be improved simultaneously with increased oxygen pressure. As shown in figures 6 and 7, the O₂-0.12 MPa film with the flat particles reduced the electron scattering, resulting in increased conductivity. In addition, the Seebeck coefficient was increased due to the decrease in oxygen vacancies in the sample deposited at higher oxygen pressure. As a result, increasing content of singly-ionized oxygen leads to the higher power factor PF observed from the O₂-0.12 MPa film [23].

Similar to Liu's publication [23], Zhou *et al* [36] also reported the correlation between the surface morphologies and the thermoelectric performance of $Zn_{0.94}Al_{0.06}O_x$ films (GZO) thin films in which the modification of the surface morphology and roughness of GZO films were tuned through the deposition temperature T_d (573 K–873 K) during the growth of GZO thin films on Al_2O_3 (AO) single-crystal substrates. The GZO film deposited at 673 K (GZO-673-AO) exhibited the good electrical conductivity due to high carrier mobility due to good crystallinity and high carrier concentration through the Ga doping on the Zn sites. In addition, the Seebeck coefficient value of the GZO-673-AO film increases with an increase of carrier concentration and the enlarged effective mass due to the enhancements of the



Figure 4. Heavy element doping for enhancing thermoelectric properties of nanostructured zinc oxide [Reprinted with permission from [24]. Copyright 2013 Royal Society of Chemistry].

density of states. Consequently, the GZO-673-AO film has the highest power factor value of 256 μ Wm⁻¹K⁻², as shown in figure 8 [36].

4. Dual dopant doped ZnO based bulks and thin films

In general, the thermoelectric performance can be enhanced by a single doping. However, the solubility limit of the dopant in single doping limits the improvement of *ZT*. Therefore, efforts in dual doping to improve the thermoelectric properties of ZnO materials have been conducted such as Al-Mg [37], Al-Ga [13], Al-Ti [38, 39], Al-Ni [38], Sb-Sn [40], Al-In and Ga-In [41–47].

Yamaguchi *et al* reported that the thermal conductivity κ values of their AZO: Ni and AZO: Sm ceramic samples were 9.2 Wm⁻¹K⁻¹ and 17.2 Wm⁻¹K⁻¹ at room temperature,

respectively. Therefore, the AZO: Ni samples have higher ZT value of 0.126 at 1073 K [38].

Park *et al* reported that the co-doping of Al and Ti into ZnO ceramic samples $(Zn_{0.97}Al_{0.02} Ti_{0.01}O)$ has a PF of $3.8 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ at 1073 K [39]. By using different dopants (Sb and Sn), Park continued to report that the Zn_{0.985}Sb_{0.005}Sn_{0.01}O samples showed the higher PF value of $1.15 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ at the same measuring temperature 1073 K [40]. However, those values are lower than the *PF* value of $1.4 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-1}$ at 1273 K obtained from a single 2 at % Al-doped ZnO bulk [12, 17].

Toshiyuki Mori *et al* [41] suggested the reduction of thermal conductivity in Ga and In dually doped ZnO bulk due to the formation of three-dimensional stacking faults, as shown in figure 9. It was found that the (Ga_{0.004}, In_{0.004})Zn_{0.992}O bulk with dense three-dimensional stacking faults revealed the *PF* value of 7.2×10^{-4} Wm⁻¹K⁻² and a



Figure 5. The thermal conductivities of ZnO thin films as a function of the (a) Al-doping, (b) porosity, and (c) grain size of the films. The measurement was performed at 300 K. [Reprinted with permission from [22]. Copyright 2015 Elsevier].

thermal conductivity κ of 2.6 Wm⁻¹K⁻¹ resulting in ZT of 0.19 at 773 K [41].

Li *et al* [42] reported the influence of spark plasma sintering using different sintering temperatures on the microstructure and thermoelectric properties of Al, Ga dual-doped ZnO bulk. The *ZT* values of the $Zn_{0.96}Al_{0.02}Ga_{0.02}O$ bulk samples were 0.09–0.14 at the temperature range of 1073–1273 K [42].

Ohtaki et al [13] reported the highest PF of above $1 \times 10^{-3} \ {
m Wm^{-1}K^{-2}}$, the thermal conductivity κ of below 5 $Wm^{-1}K^{-1}$ and the ZT value of 0.65 at 1273 K obtained from the dual doping of ZnO ceramic samples with Al and Ga $(ZnAl_{0.02}Ga_{0.02}O)$, as shown in figure 10. The remarkable ZT value is explained through the presence of granular texture in the ZnAl_{0.02}Ga_{0.02}O nanocomposite structure, which results in reducing the thermal conductivity while maintaining high electrical conductivity [13]. Chen et al [48] proposed a reduced graphene oxide (rGO) as a new dopant added to Al doped ZnO (AZO), in which the rGO inclusions are induced in the AZO matrix, leading to multiple interfaces between AZO and rGO. Results presented in figures 11 and 12show that the lattice thermal conductivity is remarkably reduced through the phonon-boundary scattering. The extra electrons are induced in the $Zn_{1-x}Al_xO/rGO$ composites because of the capture of Zn²⁺ ions at the rGO sites, thus increasing electron density. The nanocomposites with rGO content of 1.5 wt% reached the ZT value of 0.28 at 900 °C, which is 8 times larger than that of undoped ZnO and 60% larger than the ZT of alloyed AZO [48].

Besides the dual-doped ZnO based bulk materials, thermoelectric properties of dual-doped ZnO based thin films have also been reported [43–47].

For instance, Zheng *et al* [43] reported thermoelectric properties of the In-doped AZO thin films and un-doped AZO thin films. The un-doped AZO thin film shows a relatively stronger texture and larger grain size, which suggests high electrical conductivity. However, it has a very low Seebeck

coefficient that causes poor thermoelectric properties. Based on Indium doping, the value of the Seebeck coefficient of Indoped thin films increases stably with increasing In content, the *PF* value of 2.22×10^{-4} Wm⁻¹K⁻² at room temperature is reported for 0.71 wt% In-doped AZO thin films, several times higher than that of the un-doped thin film. However, the thermal conductivity κ and *ZT* value of the In-doped AZO thin films were not reported [43].

On the other hand, Seo et al [45] reported thermoelectric properties of the InGaO₃(ZnO)_m superlattice deposited on a sapphire substrate as shown in figures 13 and 14. It is noted that the deposited single crystal IGZO thin films have poor crystallinity due to the large lattice mismatch between the IGZO thin film and sapphire substrate, leading to poor thermoelectric properties. To overcome these disadvantages, they used the ZnO as a buffer layer in order to reduce the lattice mismatch with the substrate in the InGaO₃(ZnO)_m superlattice structure, followed by plasma treatment. Consequently, the PF values were 6 \times 10⁻⁷, 7 \times 10⁻⁶ and 8 \times 10⁻⁵ Wm⁻¹K⁻² at 375 K for the as-grown, thermally annealed, and plasma treated superlattice samples, respectively. The thermal conductivities κ were 7.53, 1.00 and 1.46 $\mathrm{Wm}^{-1}\mathrm{K}^{-1}$ at room temperature for the as-grown, thermally annealed, and plasma treated superlattice samples, respectively [45].

Nguyen *et al* [46] reported thermoelectric properties of Ga and In dually doped ZnO thin films annealed at various temperatures. The thin films annealed at 500 °C, GZO@500 and IGZO@500 thin films, showed the *PF* values of 4.39×10^{-4} Wm⁻¹K⁻² and 3.09×10^{-4} Wm⁻¹K⁻², the thermal conductivity κ values of 2.2 Wm⁻¹K⁻¹ and 0.95 Wm⁻¹K⁻¹ and *ZT* values of 0.114 and 0.186, respectively. The better thermoelectric performance of the IGZO@500 thin films is explained through the Photoluminescence spectral, especially in the range of 432–510 nm: the additional zinc interstitials as point defects in the GZO@500 thin films not only enhanced the *PF* but also improved the thermal conductivity κ , resulting in lower *ZT* than the IGZO@500 thin film, as shown in figure 15 [46, 47].

Li *et al* [49] presented a joint improvement in the ZnO: Al films by tuning the diffusion of the Au layer via substrate temperature, as shown in figure 16. Due to the impact of the diffusion of the Au layer on electronic interactions, the RT-ZnO: AuAl films show the *PF* value of 3.58×10^{-5} Wm⁻¹K⁻², which is two orders of magnitude larger than that of the RT-ZnO: Au film at the same measuring temperature [49].

5. ZnO nanowires

In general, the charge transport and carrier mobility of nanowires depend strongly on their surfaces which are related to their defect densities. In addition, the surface of nanowires plays an important role in phonon scattering [50].

The challenge is how to control properly the nanowire surface characteristics to obtain the best thermoelectric properties because the increase of surface roughness could decrease the thermal conductivity and electron transport



Figure 6. AFM images and XRD patterns of the $Zn_{0.94}Al_{0.06}O_x$ films formed at different oxygen pressures. (a), (b) and (c) are the AFM results of the $O_2-0.021$ MPa, $O_2-0.1$ MPa, and $O_2-0.12$ MPa films, respectively; (d) XRD patterns of the $Zn_{0.94}Al_{0.06}O_x$ films compared with ZnO and Zn; (e) surface roughness and particle size. [Reprinted with permission from [23]. Copyright 2019 Elsevier].



Figure 7. (a) Resistivity, (b) Seebeck coefficient and (c) Power factor of the $Zn_{0.94}Al_{0.06}O_x$ films formed at different oxygen pressures. [Reprinted with permission from [23]. Copyright 2019 Elsevier].

simultaneously. However, the advantage of nanowires is quantum effects. The quantum confinement in low dimensional structures results in the increase of electronic densities of states of carriers due to the confinement. This leads to the increase of the Seebeck coefficient according to the Mott's relationship without lowering the electrical conductivity [51].

Therefore, apart from thin film and bulk materials, the ZnO nanowires are an interest of research for TE application. For example, the ZnO nanowires synthesized by thermal evaporation, possess a ZT of 0.1 at 970 K, which is much higher than that of pure ZnO bulk material, as shown in figure 17 [52].

The Ga-doped ZnO nanowires could achieve the maximum peak ZT at room temperature, which is 2.5 times higher than that of pure ZnO nanowires [53]. On the other hand, the Al and Ga co-doped ZnO nanowires could reduce the thermal conductivity to 25% over the bulk ZnO and increase the power factor due to the resonant scattering of hybridization of Al and Ga valence bands. As shown in figure 18, the *ZT* reaches 0.6 at 1273 K [54]. The experimental and theoretical studies show that the Al, Sb, Ga doped ZnO nanowires could achieve the higher TE performance, as shown in figure 19 [55].

For the In dopant, the theoretical calculation using the density functional theory (DFT) from QUANTUM ESPRESSO suite of codes shows that the In-doped ZnO nanowires provide the good electrical conductivity and lower the thermal conductivity along the wire due to the surface scattering effects [56].

Review



Figure 8. (a) *PF* values of GZO thin films deposited at 573 K to 873 K; (b) *PF* value comparison for GZO-673-AO, GZO-673-SO, AZO-673-AO and ZnO, IGZO, GZO thin films. [Reprinted with permission from [36]. Copyright 2018 Royal Society of Chemistry].

Apart from conventional doping approaches, ZnO nanowires have been studied for TE application via other ways. For example, Ishibe *et al* [57, 58] proposed the dopant controlled epitaxial interface method in which two crystal structures are coherently connected to avoid the lattice distortions or misfit dislocation to improve the power factor of materials. The ZnO NWs were grown on the ZnO buffer substrates using the PVD method and obtained the high power factor of 7 μ Wcm⁻¹K⁻² ZnO film. By introducing ZnO nanowires into ZnO film, the *PF* has been increased 3 times in comparison with that of pristine ZnO film while the thermal conductivity was reduced by increasing the phonon scattering at the nanowire interfaces, as shown in figure 20 [57, 58].

6. Summary

The potential of ZnO based materials for waste heat recovery at high temperature has been proven over the last few decades. ZnO as a high-temperature thermoelectric material suffers from high lattice thermal conductivity and poor electrical conductivity. The doping dopants lead to the introduction of point defects or nanoprecipitation or stacking/faults in the host structures, which, in turn, influence the thermoelectric performance. The presence of defects could result in either improvement or worsening of the thermoelectric properties. The dopants with heavier atomic masses compared to the Zn atom are preferred due to contributions to the decrease of lattice thermal conductivity by introducing more mass fluctuations. In addition, the smaller ionic radius of the dopant also induces smaller distortion of the host crystal structure. Among dopant elements, Al dopant seems to be effective dopant resulting in better thermoelectric properties.

It is important to note that the dual-doping approach is very promising because it can effectively reduce the thermal conductivity and simultaneously enhance the electrical conductivity. The drastic improvement of *ZT* of Al-Ga dually doped ZnO bulk or Ga-In dually doped ZnO thin films shows strong evidence of this approach.

Apart from doping to improve the thermoelectric properties, nanostructuring of ZnO and ZnO nanowires have shown great interest. The nano-constituents embedded in a matrix material or a mixture of different nano-constituents can result in the reduction of lattice thermal conductivity due to the strong phonon-interface scattering. On the other hands, it enhances the electronic performance due to the modification of electron scattering and band structures. The Seebeck coefficient and power factor could also be increased through the low-energy carrier filtering of nanostructured materials. The combination of low thermal conductivity due to doping and the high-power factor due to nanostructuring could improve the thermoelectric performance.

In addition, the low-dimensional structure such as nanowire structure is promising for improving the thermoelectric properties of materials because of their strong quantum confinement effect, which results in the increase of electronic densities of states of carriers due to the confinement. This leads to the increase of the Seebeck coefficient according to the Mott's relationship without lowering the electrical conductivity.

Acknowledgments

This work was supported by Vietnam National University Ho Chi Minh City under grant number B2018-50-02.



Figure 9. (a) TEM bright field image taken from $(Ga_{0.008}, In_{0.008})Zn_{0.984}O$ sintered sample, and SAEDP recorded from the aforementioned sample. White arrows indicate the diffuse strike in the background of SAEDP. (b) TEM dark field image taken from $(Ga_{0.008}, In_{0.008})Zn_{0.984}O$ sintered sample. B.SF: basal-plane stacking fault, P.SF.: pyramidal-plane stacking fault. [Reprinted with permission from [41]. Copyright 2014 Royal Society of Chemistry].

Notes

The authors declare no competing financial interest.



Figure 10. Temperature dependence of the dimensionless figure-ofmerit of $Zn_{1-x-y}Al_xGa_yO$ (0.02 < x < 0.04, 0 < y < 0.05) ceramics. [Reprinted with permission from [13]. Copyright 2009 Springer Nature].



Figure 11. Schematic illustration of possible mechanisms of forming the $Zn_{0.98}Al_{0.02}O/rGO$ composites as an example. [Reprinted with permission from [48]. Copyright 2015 American Chemical Society].



Figure 12. Temperature dependence of TE properties of AZO and AZO/rGO composites in the range of 25 °C–900 °C. (a) Electrical conductivity; (b) Seebeck coefficient; (c) lattice thermal conductivity, (inset) total thermal conductivity (κ); and (d) *ZT*. In graphs (a) and (b), the points are experimental data, and the fitted lines are the corresponding simulated results. In graphs (c) and (d), the lines are plotted as a guide for the eye. [Reprinted with permission from [48]. Copyright 2015 American Chemical Society].



Figure 13. Schematic models showing the reduction of lattice mismatch on the in-plane of the substrates by introducing the ZnO buffer layer: (a) InGaZnO/ sapphire substrate and (b) InGaZnO/ZnO/sapphire substrate. [Reprinted with permission from [45]. Copyright 2011 Elsevier].



Figure 14. Plots of thermoelectric properties as a function of measured temperature for the as-deposited (black square), thermally annealed in 900 °C for 9 h (red circle), and thermally annealed and Ar plasma treated (blue triangle) SAM2. (a) Electrical resistivity, (b) Seebeck coefficient, and (c) thermoelectric power factor. (d) The plot of temperature rise per input power (inset table: calculated thermal conductivities). [Reprinted with permission from [45]. Copyright 2011 Elsevier].



Figure 15. Effect of annealing temperature on thermoelectric properties of Ga and In dually doped ZnO thin films [Reprinted with permission from [47]. Copyright 2018 Elsevier].



Review

Figure 16. Joint improvement of conductivity and Seebeck coefficient in the ZnO:Al thermoelectric films by tuning the diffusion of Au layer [Reprinted with permission from [49]. Copyright 2018 Elsevier].



Figure 17. The Seebeck coefficient and *ZT* value of ZnO NW as a function of temperature [Reprinted with permission from [52]. Copyright 2011 WILEY-VCH Verlag GmbH & Co.KGaA, Weinheim].



Figure 18. Engineering efficient thermoelectrics from large-scale assemblies of doped ZnO nanowires: nanoscale effects and resonant-level scattering [Reprinted with permission from [54]. Copyright 2014 American Chemical Society].



Figure 19. (a) The electrical conductivity s, (b) Seebeck coefficient *S*, (c) power factor *PF*, and (d) figure of merit *ZT* of Al, Ga, Sb doped ZnO nanowires with the change in temperature [Reprinted with permission from [55]. Copyright 2013 Royal Society of Chemistry].



Figure 20. The methodology of thermoelectric power factor enhancement by controlling nanowire interface [Reprinted with permission from [58]. Copyright 2018 American Chemical Society].

References

- [1] Rowe D M 2006 CRC Handbook of Thermoelectrics: Macro to Nano (Boca Raton, FL: CRC Press) (https://doi.org/ 10.1201/9781420038903)
- [2] Heremans JP, Wiendlocha B and Chamoire A M 2012 Environ. Sci. 5 5510
- [3] Wang H, Gibbs Z M, Takagiwa Y and Snyder G J 2014 Energy. Environ. Sci. 7 804
- [4] Zhao L D et al 2013 J. Am. Chem. Soc. 135 7364
- [5] Ohtaki M 2011 J. Cera. Soc. Japan 119 770
- [6] Zhao Y, Yan Y, Kumar A, Wang H, Porter W D and Priya S 2012 J. Appl. Phys. 112 034313
- [7] Han L, Nong N V, Hung L T, Holgate T, Pryds N, Ohtaki M and Linderoth S 2013 J. Alloys Compd. 555 291
- [8] Nag A and Shubha V 2014 J. Electron. Mater. 43 962
- [9] Nong N V and Pryds N 2013 Adv. Nat. Sci.: Nanosci. Nanotechnol. 4 023002

- [10] Özgür Ü, Alivov Y I, Liu C, Teke A, Reshchikov M A, Doğan S, Avrutin V, Cho S J and Morkoç H 2005 J. App. Phys. 98 041301
- [11] Ren G, Lan J, Zeng C, Liu Y, Zhan B, Butt S, Lin Y-H and Nan C-W 2015 JOM 67 211
- [12] Ohtaki M, Tsubota T, Eguchi K and Arai H 1996 J. Appl. Phys. 79 1816
- [13] Ohtaki M, Araki K and Yamamoto K 2009 J. Electronic Materials. 38 1234
- [14] Jood P, Mehta R J, Zhang Y, Peleckis G, Wang X, Siegel R W, Borca-Tasciuc T, Dou S X and Ramanath G 2011 Nano Lett. 11 4337
- [15] Martin S, Espen D B, Kasper A B, Sebastian C, Mogens C and Bo B I 2013 Acta Materialia. 61 3314
- [16] Lin W, Chen D, Zhang J, Lin Z, Huang J, Li W, Wang Y and Huang F 2009 Cryst. Growth Des. 9 4378
- [17] Tsubota T, Ohtaki M, Eguchi K and Arai H 1997 J. Mater. Chem. 7 85
- [18] Nam W H, Lim Y S, Choi S-M, Seo W-S and Lee J Y 2012 J. Mater. Chem. 22 14633
- [19] Zhao Y, Chen B, Miner A and Priya S 2014 RSC Adv. 4 18370
- [20] Han L, Nong N V, Zhang W, Hung L T, Holgate T, Tashiro K, Ohtaki M, Pryds N and Linderoth S 2014 RSC Adv. 4 12353
- [21] Zhang D-B, Li H-Z, Zhang B-P, Liang D-D and Xia M 2017 RSC Adv. 7 10855
- [22] Park T-H, Park N-W, Kim J, Lee W-Y, Koh J-H and Lee S-K 2015 J. Alloys Compd. 638 83
- [23] Liu S, Li G, Piao Y, Chang L, Gao Y and Wang Q 2019 J. Phys. Chem. Solids 124 13
- [24] Jood P, Mehta R J, Zhang Y, Tasciuc T B, Dou S X, Singh D J and Ramanath G 2014 RSC Adv. 4 6363
- [25] Ohta H, Seo W S and Koumoto K 1996 J. Am. Ceram. Soc. 79 2193
- [26] Minami T, Kakumu T and Takata S 1996 VAC Sci. Technol. A 14 1704
- [27] Orikasa Y, Hayashi N and Muranaka S 2008 J. Appl. Phys. 103 113703
- [28] Hopper E M, Zhu Q, Song J H, Peng H, Freeman A J and Mason T O 2011 J. Appl. Phys. 109 013713
- [29] Sawalha A, Abu-Abdeen M and Sedky A 2009 Physica B: Condensed Matter 404 1316
- [30] Park K, Seong J K and Kim G H 2009 J. Alloys Compd. 473 423
- [31] Colder H, Guilmeau E, Harnois C, Marine S, Retoux R and Savary E 2011 J. Eur. Ceram. Soc. 31 2957
- [32] Park K, Seong J K and Nahm S 2008 J. Alloys Compd. 455 331
- [33] Park K, Seong J K, Jwon S Y, Nahm S and Cho W S 2008 Mater. Res. Bull. 43 54

- [34] Paulson A, Sabeer N A M and Pradyumnan P P 2019 J. Alloys Compd. 786 581
- [35] Jung K-H, Lee K H, Seo W-S and Choi S-M 2012 Appl. Phys. Lett. 100 253902
- [36] Zhou Z, Ren G, Tan X, Liu R, Liu C, Lin Y H and Nan C 2018 Mater. Chem. A 6 24128
- [37] Tsubota T, Ohtaki M, Eguchi K and Arai H 1998 J. Mater. Chem. 8 409
- [38] Yamaguchi H, Chonan Y, Oda M, Komiyama T, Aoyama T and Sugiyama S 2011 J. Electron. Mater. 40 723–7
- [39] Park K, Ko K Y, Seo W S, Cho W S, Kim J G and Kim J Y 2007 J. Eur. Ceram. Soc. 27 813
- [40] Park K and Seong J K 2008 J. Alloys Compd. 464 1
- [41] Takemoto H, Fugane K, Yan P, Drennan J, Saito M, Mori T and Yamamura H 2014 RSC Adv. 4 2661
- [42] Li H, Le T H, Ngo V N, Nini P and Søren L 2013 J. Elec. Mater. 42 1573
- [43] Zheng Z H, Fan P, Luo J T, Liang G X and Zhang D P 2015 Electro. Mater. Lett. 11 429
- [44] Teehan S, Efstathiadis H and Haldar P 2011 J. Alloys Compd. 509 1094
- [45] Seo D K, Shin S W, Cho H H, Kong B H, Whang D M and Cho H K 2011 Acta. Mater. 59 6743
- [46] Nguyen N H T et al 2016 ACS Appl. Mater. Interfaces 8 33916e33923
- [47] Pham A T T et al 2018 J. Alloys Compd. 747 156
- [48] Chen D, Zhao Y, Chen Y, Wang B, Chen H, Zhou J and Liang Z 2015 ACS Appl. Mater. Interfaces 7 3224
- [49] Li G, Liu S, Piao Y, Jia B, Yuan Y and Wang Q 2018 Mater. Des. 154 41
- [50] Schmidt V, Wittemann I V, Senz S and Gösele U 2009 Adv. Mater. 21 2681
- [51] Mao J, Liu Z and Ren Z 2016 NPJ Quantum Mater. 1 16028
- [52] Liu Y, Zhang Zh, Wei X, Li Q and Peng L-M 2011 Adv. Funct. Mater. 21 3900
- [53] Shi L, Chen J, Zhang G and Li B 2012 Phys. Lett. A 376 978
- [54] Brockway L, Vasiraju V, Sunkara M K and Vaddiraju S 2014
- ACS Appl. Mater. Interfaces 6 14923
 [55] Wang C, Wang Y, Zhang G, Peng C and Yang G 2014 Phys. Chem. Chem. Phys. 16 3771
- [56] Catellani A, Ruini A, Nardelli M B and Calzolari A 2015 RSC Adv. 5 44865
- [57] Ishibe T, Tomeda A, Watanabe K, Kamakura Y, Mori N, Naruse N, Mera Y, Yamashita Y and Nakamura Y 2017 *Journal of Elec. Materi.* 46 3020
- [58] Ishibe T, Tomeda A, Watanabe K, Kamakura Y, Mori N, Naruse N, Mera Y, Yamashita Y and Nakamura Y 2018 ACS Appl. Mater. Interfaces 10 37709