The effect of Bi doping on the thermal conductivity of ZnO and ZnO:Al thin films

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ABSTRACT

The dissipation of heat generation has been one of the largest obstacles in the design of semiconductor devices and reducing the thermal conductivity is vital for improving thermoelectric efficiency. This work focuses on the Bi doping effect on ZnO, and ZnO:Al thin films produced by magnetron sputtering with thickness varying between 500 and 900 nm. The approach introduces Bi ions, a higher mass element, into the ZnO metal-oxide matrix, to hinder phonon-mediated heat conduction and, consequently, reduce thermal conductivity. Atom probe tomography (APT) was employed to survey Bi doping distribution in ZnO:Al:Bi and ZnO:Bi thin films and to study the morphology of the grain boundaries. The thermal properties of the thin films were measured by frequency-domain thermoreflectance. Based on thermal conductivity results, it is concluded that the doping of ZnO films with Al has a significant effect on thermal conductivity, being reduced from 6.0 W m⁻¹ K⁻¹ in its undoped state to 3.3 W m⁻¹ K⁻¹ for ZnO with ~3 at.% of Al, mainly due to alloy scattering of phonons in the wurtzite cell. Further doping with Bi contributes to a slight reduction in the thermal conductivity of ZnO:Al:Bi films (2.9 W m⁻¹ K⁻¹), due to grain boundary scattering by Bi/Bi₂O₃ phases. This result is understood as the confluence of two counteracting effects. On the one hand, the thermal conductivity of the film decreases because Bi, unlike Al, is segregated to grain boundaries and does not substitute Zn in the wurtzite crystal lattice, which is unequivocally demonstrated by APT results. On the other hand, the simultaneous presence of Al and Bi triggers a morphological change with the film’s microstructure becoming more columnar. This change in microstructure from 3D island growth in ZnO:Al and ZnO:Bi to a more regular columnar structure in ZnO:Al,Bi limits further reduction in the thermal conductivity.

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1. Introduction

The direct energy conversion between the transport of heat and electric charge based on thermoelectric effects has been a topic of long-standing interest in condensed matter materials science for over half a century [1]. The dissipation of heat generation has been one of the most significant obstacles in the design of semiconductor devices [2–4]. It is possible to control heat propagation by engineering the phononic properties of thermoelectric materials, where phonons are the main heat carriers and materials with low thermal conductivities are desired [3]. An effective strategy to obtain high thermoelectric efficiency is to lower the lattice thermal conductivity [5,6]. K.B. Spooner et al. [7] used hybrid density functional theory to demonstrate that reducing the lattice thermal conductivity is vital for improving the thermoelectric efficiency in transparent conducting oxides (TCO).

Zinc oxide is a heteropolar II-VI semiconductor with interesting physical-chemical properties that has drawn attention to several fields of research and applications. It is an interesting choice due to its low cost and relatively low deposition temperature, stability in hydrogen plasma, abundancy as a raw material and non-toxicity [8]. ZnO crystallizes in the hexagonal wurtzite structure and displays an intrinsic low n-type electrical conductivity. This, allied with its high transparency and direct

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candidates for applications as TCOs, some authors have reported inter
magnitude [20]. These films were deposited on Si substrates with
thermal conductivity as high as 60 W m\(^{-1}\)K\(^{-1}\)
for testing thermoelectric properties as well [23]. Among such as Aluminium (Al), which has n-type carrier concentration, the
electrical conductivity can be increased by more than 3-4 orders of
magnitude [20–22]. Besides the fact that doped ZnO films are prominent
candidates for applications as TCOs, some authors have reported interesting
thermoelectric properties as well [23–25]. Bulk ZnO features a
thermal conductivity as high as 60 W m\(^{-1}\)K\(^{-1}\) that can be lowered with
doping or nano-structuring strategies [7,26]. For Al-doped ZnO thin
films at room temperature, T.-H. Park et al. [27] obtained average
thermal conductivities in the range of 1.1–5.6 W m\(^{-1}\)K\(^{-1}\), while Loureiro
et al. [28] obtained a thermal conductivity lower than 1.2 W m\(^{-1}\) K\(^{-1}\).

In this work, transparent ZnO, ZnO:Bi, ZnO:Al and ZnO:Al:Bi thin
crystalline structures, d) Bi content, which includes Bi and Bi
species.

Fig. 1. Side view of the 3D reconstruction obtained by Atom Probe Tomography of a tip of the ZnO:Al:Bi sample with ~1 at.% of Bi. a) Zn content, b) O content, c) Al
crystalline structures, d) Bi content, which includes Bi and Bi
species.

band-gap of ~3.4 eV at room temperature, grants optoelectronic
applicability in the near-UV range, such as for photodetectors,
light-emitting diodes, photovoltaics, gas sensing and thin-film transis-
tors [9–19], etc. Furthermore, by doping ZnO with Group IIIB elements
such as Aluminium (Al), which has n-type carrier concentration, the
electrical conductivity can be increased by more than 3-4 orders of
magnitude [20–22]. Besides the fact that doped ZnO films are prominent
candidates for applications as TCOs, some authors have reported interesting
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modelled numerically, solving the parabolic heat equation for the described geometry. The model used to fit the phase lag curve describes the behaviour of a stack of layers composed by the Au transducer, the undoped and doped ZnO films, the substrate, and an effective thermal boundary conductance that accounts for the two interfaces between the different layers \[31,32\]. One of the adjustable parameters obtained by least-squares fitting is the out-of-plane thermal conductivity.

3. Results and discussion

Figs. 1 and 2 show the reconstructions of a ZnO:Al,Bi film deposited with approximately ~1 at.% of Bi content, observed laterally and from the top in relation to the film growth direction, respectively. For the top-view (Fig. 2), due to the cone-shape of the APT tip, leading to an apparent inhomogeneity at the center of the reconstruction, the reconstruction was sliced to display the 60–120 nm region in the z-direction. The estimation of the Bi content in the samples is based on a compositional analysis by RBS, XPS and EDX studies on similar films previously published by the authors \[30\].

In the various side views of the ZnO:Al,Bi sample in Fig. 1, it can be seen that both the matrix elements, Zinc (in grey), Oxygen (in blue), and the Aluminium dopant (in green), are homogeneously distributed throughout the sample. Conversely, the Bi dopant (in red) is more concentrated along three vertical lines. From observing the top views of the same sample (Fig. 2), one can see that both the matrix elements, Zn and O, and the dopant Al, are homogeneously distributed. Again, contrariwise, the distribution of Bi is heterogeneous. From the conjugation of the two views, or rather, the projections of the Bi concentration shown, it is concluded that Bi appears to segregate at the triple points of the grain boundaries and not in all of the boundary surface, as one does.
not observe Bi-rich planes but lines. These conclusions are coherent with results already published by the authors [33], according to what was found by transmission electron microscopy (TEM) about very similar samples of ZnO:Ga,Bi. The TEM micrographs in this referred work can be regarded as a sectional analysis according to the xy plane, and coherently with what has been discussed about the APT results, it is possible to conclude that the concentration of Bi is higher at the triple points. This fact reinforces that Bi segregates in the triple points forming small columns, perpendicular to the sample surface. For the case of ZnO:Bi (without Al doping) the APT reconstruction of a sample with ~1 at.% of Bi is shown in Figs. 3 and 4, where the atomic distribution of Zn, O and Bi is homogeneous, hence the segregation of Bi is not observed. Same as before, the top-view (Fig. 4) reconstruction was sliced to display the 165–350 nm region in the z-direction.

From the analysis of the SEM micrographs in Fig. 5 for a) ZnO, b) ZnO:Al, c) ZnO:Bi and d) ZnO:Al,Bi films, two conclusions can be made. First, it can be seen that the introduction of Bi in ZnO:Al causes a change in its morphology to a more columnar type. The same is seen in the ZnO samples but in a much less pronounced way. This observation is corroborated by the X-ray diffraction (XRD) results previously published by the authors [25]. Second, the cross-section morphology for ZnO:Al,Bi is more columnar than that of ZnO:Bi. In short, Bi doping seems to promote the columnar growth of the films and is enhanced by the presence of Al. An explanation for why Bi segregation is not observed in the APT topographies for ZnO:Bi films, resides in the fact that ZnO:Al,Bi films are more texturized along [001], when compared to ZnO:Bi, which has a more 3-dimensional growth. Moreover, the triple points are well vertically aligned in ZnO:Al,Bi grains, contrariwise to ZnO:Bi where triple points may not follow a line.

Fig. 4. Top view of the 3D reconstruction obtained by Atom Probe Tomography of a tip of the ZnO:Bi sample with ~1 at.% of Bi, sliced to display the 165–350 nm region in the z-direction. a) Zn content, b) O content, c) Bi content, which includes Bi and Bi$_2$O$_3$ species.

Fig. 5. Scanning electron microscopy cross-sectional micrographs for a) ZnO, b) ZnO:Al, c) ZnO:Bi and d) ZnO:Al,Bi films.

Fig. 6 presents the results of the out-of-plane thermal conductivity
The error bar represents the sets of values of \( \kappa \) that produce a fit within an acceptable error margin, as shown in Fig. 7. Bi doping in ZnO promotes a significant decrease in \( \kappa \), from 6.0 W m\(^{-1}\) K\(^{-1}\) to 3.4 W m\(^{-1}\) K\(^{-1}\), which is not the case with the Bi doping in ZnO:Al films (from 3.3 to 2.9 W m\(^{-1}\) K\(^{-1}\), where \( \kappa \) seems unaffected considering the error margin (\( \pm 0.3 \) W m\(^{-1}\) K\(^{-1}\)). Another fact is that ZnO:Al has a lower electrical conductivity when compared to undoped ZnO [25]. It is well known that the thermal conductivity of polycrystalline thin films is always significantly lower compared to that of bulk materials [34]. Moreover, this property depends on film morphology and thickness of the layer, especially for thickness below 1 \( \mu \)m [35,36]. The main origin of this phenomenon is the intense increase in the density of grain boundaries and their respective deterioration and, for smaller film thickness, the surface roughness effects. Thus, for the case of the samples with ZnO matrix, morphological reasons linked to the presence (ZnO:Bi) or absence (ZnO) of Bi/Bi\(_2\)O\(_3\) at the triple points of the grain boundaries are sought to justify the \( \kappa \) decrease. As the authors have previously proven that Bi does not enter the ZnO crystal lattice [33], then \( \kappa \) decreases due to the inherent phonon scattering from Bi/Bi\(_2\)O\(_3\) at the triple points of the grain boundaries. Curiously, the more pronounced change in morphology from ZnO:Al to ZnO:Al,Bi does not affect significantly \( \kappa \); albeit reducing by 0.4 W m\(^{-1}\) K\(^{-1}\). Alloying ZnO with Al causes a reduction by approximately half of \( \kappa \) due to alloy scattering of the ZnO phonons. Alloying ZnO with Bi causes a similar reduction in \( \kappa \) as for Al. This is at first surprising, because Bi is not incorporated in the ZnO...
lattice but segregates to the grain boundaries (mainly the triple points). This means that grain boundary scattering is enhanced by Bi incorporation, up to a point of causing a similar effect as alloy scattering with Al in ZnO. There might be a small contribution from the small change in morphology, leading to the enhanced columnar structure. Thus, the change in microstructure from 3D island growth in ZnO:Al and ZnO:Bi to a more regular columnar structure in ZnO:Al,Bi limits further reduction in the thermal conductivity.

4. Conclusions

From APT reconstructions, Zn, O and Al are homogeneously distributed within the crystals (~30 nm), unlike Bi, which was not incorporated into the ZnO wurtzite cell. The Bi distribution is heterogeneous and it segregates at the triple points of the grain boundaries, also inducing the formation of thin columns perpendicular to the surface of the sample in the ZnO:Al,Bi case. Thus, Bi contributes to grain boundary scattering of phonons. A large reduction in thermal conductivity was registered from 6.0 W m⁻¹ K⁻¹ to 3.3 W m⁻¹ K⁻¹ upon alloying ZnO with ~3 at.% of Al. Bi doping (~1 at.%) contributes to only a slight reduction in the thermal conductivity of ZnO:Al,Bi films (2.9 W m⁻¹ K⁻¹), when compared to that of ZnO:Al films (3.3 W m⁻¹ K⁻¹). This means that grain boundary scattering is enhanced by Bi incorporation, up to a point of causing a similar effect as alloy scattering with Al in ZnO. The change in microstructure from 3D island growth in ZnO:Al and ZnO:Bi to a more regular columnar structure in ZnO:Al,Bi limits further reduction in the thermal conductivity.

CRediT authorship contribution statement

Filipe C. Correia: Writing – review & editing, Writing – original draft, Software, Investigation, Data curation. Joana M. Ribeiro: Writing – review & editing, Writing – original draft, Investigation, Data curation. Armando Ferreira: Writing – review & editing, Funding acquisition. J. Sebastián Reparaz: Software, Investigation, Conceptualization. Alejandro R. Goni: Writing – review & editing, Visualization, Validation, Supervision, Resources, Funding acquisition, Formal analysis, Conceptualization. Torben Bold: Writing – review & editing, Writing – original draft, Supervision, Software, Resources, Methodology, Investigation, Funding acquisition. Adelio Mendes: Supervision, Funding acquisition, Formal analysis. Carlos J. Tavares: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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