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Crystal orientation dependent thermoelectric properties of highly oriented aluminum-doped zinc oxide thin films

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We demonstrate that the thermoelectric properties of highly oriented Al-doped zinc oxide (AZO) thin films can be improved by controlling their crystal orientation. The crystal orientation of the AZO films was changed by changing the temperature of the laser deposition process on LaAlO₃ (100) substrates. The change in surface termination of the LaAlO₃ substrate with temperature induces a change in AZO film orientation. The anisotropic nature of electrical conductivity and Seebeck coefficient of the AZO films showed a favored thermoelectric performance in c-axis oriented films. These films gave the highest power factor of 0.26 W m⁻¹ K⁻¹ at 740 K. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4790644>]

Zinc oxide (ZnO) has attracted considerable attention in many applications as a semiconductor oxide due to its abundance, non-toxicity, and low cost. ZnO is a wide band gap semiconductor with a direct band gap of 3.3 eV at room temperature.¹ The electrical properties of ZnO can be changed from insulator through *n*-type semiconductor to metal by controlling its doping level, while maintaining optical transparency, which makes it useful for transparent electrodes in flat-panel displays and solar cells. In addition, ZnO has better stability at high temperature than the conventional thermoelectric materials (such as Bi₂Te₃ and PbTe), which can readily oxidize in such atmospheres. Owing to its superior stability compared to those heavy metal based compounds, ZnO has potential for high temperature thermoelectric energy conversion. ZnO-based oxide thermoelectric materials show a relatively high thermoelectric power factor, *PF* (power factor in units of W m⁻¹ K⁻¹ is taken as the numerator of the figure of merit *ZT*, $ZT = (\sigma S^2 T) / \lambda$, where σ is the electrical conductivity, S is the absolute Seebeck coefficient, T is the absolute temperature, and λ is the thermal conductivity), which is competitive to the conventional thermoelectric materials. Undoped ZnO is an *n*-type semiconductor. However, by doping with Al, σ can be increased by more than three orders of magnitude at room temperature, changing the conduction behavior from semiconducting to metallic.² However, the overall thermoelectric performance of Al-doped zinc oxide (AZO) is relatively low because of its high λ .³ Therefore, enhancing the electronic transport is crucial for improving the thermoelectric properties of AZO films. Unfortunately, possible improvement in electron transport properties is often limited by the trade-off between σ and S . For example, high σ up to 7×10^3 S cm⁻¹ was reported for Ga-doped ZnO epitaxial films prepared by pulsed laser deposition (PLD), but with a low S around -11 μ V/K,⁴ whereas a high S of -140 μ V K⁻¹ was reported for PLD-grown amorphous ZnO films, but with a low σ of 100 S cm⁻¹.⁵ Optimizing the growth conditions is hence important to improve the thermoelectric power factor of ZnO-based thin films.

It is known that ZnO has an anisotropic electrical transport because of the ionic nature of the Zn–O bond and because of its wurtzite crystal structure, which lacks inversion symmetry. Thus, it may be possible to obtain better electrical transport and thermoelectric properties using ZnO-based films with specific crystal orientations. It has been reported that the in-plane electrical transport in the c-axis oriented ZnO films is enhanced compared to the a-axis oriented ones.^{6–8} A number of methods can be used to change the crystal orientation of ZnO. For example, SrTiO₃ single crystal substrates with different orientations can be used to alter the crystal orientation of PLD-grown ZnO films.⁶ The crystal orientation of AZO ceramics can also be controlled by applying a high magnetic field.⁷

In this work, we have altered the crystal orientation of AZO films on LaAlO₃ (LAO) substrates, by changing the substrate temperature (T_s) and for doing so, we have used a well-known effect whereby the surface termination of LAO substrates change at different temperatures.⁹ In this approach, the same substrate material can be used, which has the advantage that any variations in the thermoelectric properties of the AZO films are largely driven by the change in the film orientation itself, and not by interactions with the substrate material.

AZO films were deposited by PLD (Neocera, Beltsville, MD) using a KrF excimer laser ($\lambda = 248$ nm, pulse duration ~ 20 ns, repetition rate = 10 Hz). Films were deposited by ablation of a 4 N purity Al₂O₃ (2 wt. %) doped ZnO target at laser fluence of 3 J cm⁻² pulse⁻¹. The target was held on a rotating carousel to ensure a uniform ablation. In order to create sufficient oxygen vacancies and increase carrier concentration in the films, 20 mTorr of Ar was introduced as a reducing gas, using a mass flow controller. Films were deposited on (100) oriented LAO substrates (MTI corporation, USA) of dimensions 10 × 10 × 0.5 mm³ with $a_{\text{LAO}} = 3.82$ Å, held at different T_s values of 300, 425, 600, 800, and 1000 K and are denoted as films A, B, C, D, and E, respectively. The thickness of the films was around 100 nm as measured by a spectroscopic ellipsometer. The phase purity of the films was determined from the analysis of θ -2 θ (Bragg-Brentano) scan using an x-ray diffractometer (D8 Bruker, AXS System,

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Germany). ϕ -scan was done for an asymmetric (110) and (100) diffraction of the LAO substrate and AZO film, respectively. When ψ , the tilt angle of the surface normal of the film, was 45° and 2θ was fixed at 33.4° , and when ψ was 30° and 2θ was fixed at 31.77° , the respective ϕ -scans for LAO and AZO were obtained by rotating the film (0° – 360°) around the surface normal. σ and S were measured, on the same sample, from 300 to 740 K using, respectively, the linear four-probe and the differential methods, under Ar/H₂ (4% H₂ and 96% Ar) ambient using a commercial setup (RZ2001i, Ozawa Science Co Ltd., Nagoya, Japan). At any temperature, σ was measured first, followed by S by introducing a ΔT of ~ 4 – 10 K, between the voltage probes. The measurements of σ and S were then repeated at a higher sample temperature, thereby enabling studies on change in transport properties during heating. Room temperature Hall effect measurements were carried out using a physical property measurement system (PPMS) (Quantum Design, Inc., USA). The surface morphology of the films was obtained using an atomic force microscope (AFM) (Agilent, 5400, USA).

Figure 1 shows θ - 2θ x-ray diffraction (XRD) patterns for the AZO films. The patterns confirm that AZO films with a wurtzite crystal structure (Fig. 2(a)) are formed irrespective of T_s . The diffraction peaks of the (100) planes from the LAO substrate (marked “S”) and two reflections from AZO planes can be seen. Small diffraction peaks (marked by asterisk) are observed in all patterns at 52.55° which can be attributed to small concentration of secondary phases (Al₂O₃ (024)). However, since the intensity of this reflection is small and similar for all the films, the effect of the secondary phases in determining the properties is neglected. Film A has a very small peak corresponding to the (002) reflection compared to film B (marked by the arrow), indicating that the growth direction is preferentially oriented along the c-axis (c-AZO) and film A is less crystallized compared to film B. This should not be surprising since film A was deposited without substrate heating (at 300 K). On the other hand, films C and E have a single peak corresponding to (110), which indicates a growth along the a-axis (a-AZO). Film D exhibits

FIG. 1. θ - 2θ XRD pattern for AZO thin films grown on LAO substrate at different temperatures $T_s = 300, 425, 600, 800$, and 1000 K which are denoted as films A, B, C, D, and E, respectively.

both (002) and (110) orientations. The dependence of crystal orientation of the AZO films on T_s can be attributed to the change in surface termination of the LAO substrate with temperature. LAO has a layered crystal structure with alternating La–O and Al–O planes. It has been clearly demonstrated⁹ that depending on temperature, the surface termination of LAO varies. From 300 K to ~ 423 K, the surface is terminated by the Al–O plane while at temperatures above ~ 523 K, the termination is by the La–O plane. Mixed terminations containing Al, La, and O have been reported in the intermediate region of 423–523 K. The O–O bonding distances in the Al–O and La–O terminated planes on LAO (100) are 2.68 and 5.36 Å, respectively,¹⁰ while the lattice constants of AZO are $a_{\text{AZO}} = 3.25$ Å and $c_{\text{AZO}} = 5.2$ Å. If the O sites on LAO surface provide the base for Zn atoms of ZnO, one expects that the La–O terminated surface provides better match (3%–5% lattice mismatch) for the growth of a-AZO at temperatures above 550 K (Fig. 2(b)) as compared to the Al–O terminated surface because of the large lattice mismatch (94%). Also, growth of c-AZO is favored on Al–O surface, which occurs below 450 K (Fig. 2(c)).¹⁰ The mixed orientation in film D is related to the formation of oxygen vacancies in the films at $T_s > 600$ K (an effect which will be discussed in detail later), which tends to relax¹¹ the lattice causing the occurrence of both types of growth directions. The lattice constants obtained from XRD analysis are shown in Table I. However, it has been reported^{10,12} that mixed orientation of PLD-grown ZnO films can be obtained at different ranges of T_s . In these reports, the ambient gas used (20–30 mTorr of O₂) was different compared to ours (20 mTorr of Ar). The physical properties of our films must hence be expected to be different compared to the reported

FIG. 2. (a) ZnO wurtzite crystal structure with the (002) and (110) planes highlighted. (b) Lattice arrangement at the interface between (b) a-AZO film and La–O terminated LAO surface and (c) c-AZO film and Al–O terminated LAO surface. (d) XRD ϕ -scan for {100} of film C and film E (both a-AZO) and {110} of LAO substrate.

TABLE I. Measured and calculated transport properties of AZO thin films at 300 K for different substrate temperatures. The films were grown at different substrate temperatures, $T_s = 300, 425, 600, 800$, and 1000 K and are denoted by A, B, C, D, and E, respectively. Except in columns 5 and 7, the values shown are for the as-grown films. The calculated crystallite size for film D is reported, respectively, for c-AZO and a-AZO, for both as-grown and annealed films.

Sample	Lattice constant		Crystallite size		Carrier concentration ($\text{cm}^{-3} \times 10^{20}$)	Carrier concentration ($\text{cm}^{-3} \times 10^{20}$) (annealed)	Electrical conductivity (S cm^{-1})	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Seebeck coefficient ($\mu\text{V K}^{-1}$)	Power factor ($\text{W m}^{-1} \text{K}^{-1}$)
	a ($\text{\AA}$)	c ($\text{\AA}$)	($\text{\AA}$)	(Annealed) ($\text{\AA}$)						
A	...	5.205	220	250	7.90	8.85	154	1.22	-30	0.004
B	...	5.202	250	290	12.3	28.8	941	4.78	-25	0.018
C	3.244	...	190	210	1.74	4.82	207	7.43	-33	0.007
D	3.259	5.214	200, 160	210, 180	5.33	7.84	387	4.54	-30	0.011
E	3.252	...	150	170	5.26	5.56	461	5.48	-33	0.015

ones, since ambient gas for the PLD process is a crucial parameter that changes the physical properties of oxide films.¹³

Figure 2(d) shows the ϕ -scan patterns for LAO substrate and films C and E (both, a-AZO), wherein four peaks with almost equal intensity, and spaced by 90° can be observed, indicating a highly textured growth. The shift in peak positions of the ϕ -scan patterns corresponding to a-AZO {100} and LAO {110} is 45° , indicating that these two families of planes intersect the substrate surface with an angular difference of 45° . Therefore, the epitaxial relationships for a-AZO are $[001] \text{ AZO} \parallel [110] \text{ LAO}$ and $[001] \text{ AZO} \parallel [-110] \text{ LAO}$, as shown in Fig. 2(b). It is evident that films C and E, which were grown, respectively, at 600 and 1000 K, have the same in-plane epitaxy. However, the respective full width at half maximum (FWHM) values of the peaks of ϕ -scan patterns of films C and E are 5.3° and 4.35° , indicating that film E is more textured than film C. For the c-AZO films, the ϕ -scans, despite repeated attempts at different tilt angles, did not show any peaks, indicating that the crystallites are randomly distributed in the plane of the LAO substrate while maintaining their c-axis perpendicular to the substrate surface (Fig. 2(c)). The presence of a single (002) peak in the θ - 2θ scan and the absence of any peaks in the ϕ -scan indicate that film B is fibre-textured. Fibre-texture arises when the c-axis of the film is fixed perpendicular to the substrate, but the in-plane axes are randomly rotated.¹⁴ However, a ring pattern expected for fibre-textured films was not observed in the pole figures for {101} poles, which occur at ψ of 61.6° , which may be attributed to the low crystallinity of the films.

The σ - T dependence of AZO films deposited at different T_s is plotted in Fig. 3. Since the LAO substrate is insulating even after the film deposition (as measured from the rear side), its contribution to σ of AZO films can be neglected. Thus, the two possible sources for electronic charge carriers in the films are oxygen vacancies in AZO and the substitutional doping of Al^{3+} ions on the Zn^{2+} sites. Due to the presence of the charge carriers in the conduction band, all films exhibit semiconductor characteristics, with σ increasing with temperature. The most prominent feature seen in Fig. 3 is the dependence of σ on the crystal orientation. Compared to the a-AZO films, the c-AZO film (film B) shows higher σ in the entire range of temperature. However, film A, though also c-oriented, exhibits the lowest σ at 300 K, as shown in Fig. 3, possibly due to significant electron scattering, owing

to the incomplete crystallization, as may be expected for room temperature laser deposition. Furthermore, film A has the lowest electrical mobility (Table I) which is also expected. It is well known that the electron effective mass is strongly dependent on the conduction direction in anisotropic crystals. For example, electrons have higher effective mass along c-axis than along a-axis in ZnO crystals.⁸ The origin of this anisotropy is the lack of inversion symmetry and the ionic nature of the Zn-O bond, which results in a strong spontaneous bound polarization¹⁵ along c-axis, the direction along which the Zn and O atoms are stacked alternately. This polarization can generate bound positive and negative charges on (001) Zn-polar and (00-1) O-polar surfaces, respectively. These bound polarization charges induce a Schottky barrier potential at every Zn-polar surfaces which reduce effective mass and σ along the c-axis.^{6,16} It has also been found¹⁷ that though both c-polar planes and a-planes in ZnO accumulate electrons, owing to the spontaneous polarization the former accumulates more electrons. Since σ and Hall effect in our films were measured in-plane, the relevant effective mass that determines the transport is the in-plane effective mass, i.e., along directions in the c-plane of c-AZO film (film B) and along directions in the a-plane of a-AZO films (films C and E). Hence, one expects higher carrier concentration in c-AZO films compared to the a-AZO films,

FIG. 3. Electrical conductivity of AZO films grown at different substrate temperatures.

which is indeed observed (Table I). Due to the combined effect of spontaneous polarization and the resultant increase in carrier concentration, c-AZO film (film B) exhibits a higher effective in-plane σ . Film C (a-AZO) has significantly lower values of σ not only due to the polarization effect along the c-axis and a resultant drop in carrier concentration, as discussed above, but also due to its small oxygen vacancy concentration, since it was deposited at $T_s = 600$ K. Compared to film C, film E was deposited at higher T_s (1000 K, which is much higher than the temperature at which oxygen vacancies are created in AZO, as explained later) and hence the contribution of oxygen vacancies to its carrier concentration is higher, resulting in a higher σ for the entire range of temperature. Film D has lower electrical mobility (and hence lower σ) than film E since it has mixed crystal orientations (i.e., both c-AZO and a-AZO), which increases the scattering of the electrons. It may be noted that for a given crystal orientation, the carrier concentration increases with T_s , due to the increase in oxygen vacancy concentration of the films. From Table I, it is also evident that the crystallite size and carrier concentration of the films increase after annealing. It may be noted that it is possible for two films with extreme crystalline qualities to have similar carrier concentration, but other transport properties will be significantly different (compare, for instance, the mobility and electrical conductivity of films A and E).

Another interesting feature observed in Fig. 3 is the gradual increase in σ for all films, in the temperature range 550–700 K, irrespective of their crystal orientations. This change in conductivity is commonplace in oxide thermoelectrics, especially when measured in a reducing ambient such as Ar/H₂, and can be attributed to the creation of additional oxygen vacancies in the AZO films.¹⁸ To prove this argument, we measured the carrier concentration (Table I) for the as-grown films and the films subjected to thermoelectric measurements (annealed) up to 740 K in Ar/H₂. All of the annealed films have higher carrier concentration compared to the as-grown ones, as a direct consequence of oxygen vacancy creation during the annealing process, with each oxygen vacancy contributing two electrons towards conduction. It is also observed that above ~ 700 K, σ decreases with temperature since the films start to deteriorate at this temperature. We have observed a drastic drop (not shown here) in the electrical conductivity (from 830 to 430 S cm⁻¹), for an AZO film annealed up to 900 K.

In thermoelectric thin films, the transport properties also depend critically on the microstructure. In order to differentiate between the effect of crystal orientation and the possible effect of microstructure on the electrical transport, AFM images of the films were obtained. Figure 4 shows AFM phase images for film B (c-AZO), film D (a-AZO and c-AZO), and film E (a-AZO). Evidently, the surface morphology of the films is different. The rms surface roughness of the films is however nearly identical (~ 4 nm). Films B, D, and E have grain sizes around 40, 65, and 80 nm, respectively. Assuming that microstructure plays a predominant role on the transport, one would expect film B to have lower σ compared to films D and E, because of its smaller grain size, which enhances scattering and decrease mobility. But film B has the highest σ (Table I), indicating that the scatter-

FIG. 4. AFM phase images for AZO films: (a) film B (c-AZO), (b) film D (mixed orientations), and (c) film E (a-AZO).

ing of the free electrons is not dominated by grain boundaries. Hence it is clear that crystal orientation of the AZO films, and not the microstructure, plays the predominant role in determining the electrical transport properties of AZO.

The temperature dependence of Seebeck coefficient is shown in Fig. 5(a). All films have negative Seebeck coefficient indicating n -type conduction as a consequence of Al and oxygen vacancy doping of ZnO. The films (except film A) also exhibit a linear dependence of S on temperature up to around 550–600 K. Above $T \sim 600$ K, this linearity is no longer obeyed. A plausible explanation for the deviation from linearity is a change in the scattering mechanism of the free electrons. Above 600 K, oxygen vacancies are created in these oxides, as discussed earlier, which act as additional scattering centers. Film A has a different S - T dependence compared to other films, which can be explained by the enhanced electron scattering due to the low crystalline quality. Film C (a-AZO) has the highest S across the entire

FIG. 5. The temperature dependence of (a) Seebeck coefficient and (b) power factor for AZO films grown at different substrate temperatures.

temperature range compared to the other films, a result which is consistent with the fact that it also had the lowest σ . It may be noted here that the electron effective mass is higher⁸ along a-plane of AZO and the measurement of S was also done in-plane. On the other hand, film B (c-AZO) has the lowest S because of the lower electron effective mass along c-plane. In contrast, film D has lower S (lower σ) than film E (higher σ). Since film D has both types of crystal orientations, a-AZO and c-AZO, and the total electronic effective mass is a combination of the respective c-axis and a-axis components of effective mass. Therefore, the a-axis component reduces the total electron effective mass in film D, and hence results in a lower S .

The temperature dependence of the derived PF is plotted in Fig. 5(b). Film B exhibits the best PF compared to other films ($0.26 \text{ W m}^{-1} \text{ K}^{-1}$) at 740 K. The obtained value is higher

than those reported for undoped ZnO film ($0.12 \text{ W m}^{-1} \text{ K}^{-1}$)⁵ at 650 K, and Ga doped ZnO films ($2.5 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-1}$) at 300 K.⁴ The improved PF is mainly due to the enhanced electronic conductivity of the c-axis oriented film.

In summary, we showed the direct dependence of the thermoelectric properties of AZO films on crystal orientation. The crystal orientation of the AZO films can be controlled by changing the substrate temperature during deposition. To induce a change in the AZO crystal orientation, we used a well-established effect wherein LAO substrates change their surface termination at different temperatures. The c-AZO film (grown at 425 K) shows the best thermoelectric PF ($0.26 \text{ W K}^{-1} \text{ m}^{-1}$ at 740 K), which is attributed mainly to the improvement of electrical conductivity brought in by the spontaneous polarization along the c-axis, which also increases the carrier concentration. The critical dependence of thermoelectric properties on the controllable crystal orientation offers a pathway for the design of thin film thermoelectric devices using optimized AZO films.

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