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# Enhanced power factor of Indium co-doped ZnO:Al thin films deposited by RF sputtering for high temperature thermoelectrics

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ABSTRACT

An improvement in the thermoelectric power factor of Al doped ZnO has been achieved by means of co-doping with indium using a dual magnetron sputtering system. The concentration of indium in the film was varied from 0 to 10 atomic % by varying the RF power of the In target, with the ZnO:Al target fixed at 100 W. It has been found that the films with In concentrations at or below 5 at.% have no significant change in microstructure, and yet a marked improvement in thermopower. At higher doping levels, the Seebeck coefficient continues to increase, however poly-crystallinity is induced in the ZnO matrix which results in a considerable decrease in electrical conductivity. This factor ultimately has a negative impact on the materials power factor. Taking into account the films studied, $(ZnO)Al_{.03}In_{.02}$ exhibited the best thermoelectric properties with an electrical conductivity of $5.88 \times 10^2$ S/cm and a Seebeck coefficient of $-220\ \mu V/K$ at 975 K, resulting in a power factor is $22.1 \times 10^{-4}\ W m^{-1} K^{-2}$, which is three times greater than for the film with no In doping. Film microstructure, composition, and thermal stability were investigated using X-ray diffraction, scanning electron microscopy, and Auger electron spectroscopy.

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## 1. Introduction

For the past decade it has become increasingly important to search for alternative and regenerative sources of energy. For this reason, thermoelectric (TE) materials have attracted renewed attention due to their potential of harvesting huge amounts of waste heat and converting it directly into electricity. The main issue in commercializing this technology however, is the low conversion efficiency of TE materials, which is determined by the dimensionless figure of merit, $ZT = \alpha^2 \sigma T/\kappa$, where $T$ is the absolute temperature, $\alpha$ is the Seebeck coefficient, and $\sigma$ and $\kappa$ are the electrical and thermal conductivity, respectively. A limiting factor of bulk materials is that the electrical conductivity and Seebeck coefficient are inversely related, so it is not generally possible to increase the thermoelectric power factor ($\alpha^2\sigma$), i.e. thermopower, above a particular optimal value. Traditional materials ($Bi_2Te_3$ and PbTe) have only been able to achieve a $ZT$ of about 1 at 300 K, which equates to 5% efficiency [1]. In many practical applications, the TE devices can only compete with existing technologies if $ZT$ is higher than 2 [2].

With respect to high-temperature operation (>600 °C) in air applications, the investigation of metal oxide materials has rapidly progressed because they are non-toxic, thermally stable, highly resistive to oxidation, and can be fabricated using relatively simple and low cost processes. Currently, a reasonable high $ZT > 1$ has only been found in p-type oxides such as Co-based layer oxides including $NaCo_2O_4$, $Ca_3Co_4O_9$ and $Bi_2Sr_2Co_2O_y$ [3,4]. The progress in preparing n-type oxides with comparable $ZT$ has been lacking. It is known that un-doped ZnO films have n-type properties due to intrinsic defects, such as oxygen vacancies or Zn interstitials [5]. However, due to poor thermal stability and degraded electrical conductivity at higher temperatures, doping methods are necessary for better stability and adjustment of transport properties. In order to fabricate stable n-type ZnO, Group III elements (Al, Ga, and In) can be used to substitute Zn sites [6]. To date, Al doping has been the main focus of research due to its smaller atomic radius easing the site substitution mechanism. These Al-doped ZnO (AZO) films have obtained some of the best n-type bulk oxide TE measurements. The other multi-component oxides, such as ZnOGa, ZnOIn, and ZnInSnO have received attention as transparent conductive oxides (TCO's) due to their high electrical conductivities as well as high transmittances [7], but have rarely been investigated for use as TE materials.

As stated the thermoelectric power factor for a bulk material is difficult to increase due to the inverse relationship between $\alpha$ and $\sigma$. However, by co-doping with low level impurities (Al and In), we plan to achieve an increase in the density of the states by introducing multiple localized sub-bands from the impurity materials, which should lead to an increase in $\alpha$. While in parallel, the carrier electrons from the metallic dopant will play a dominant role in the film, allowing for less oxygen vacancy scattering, which will

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increase $\sigma$. Therefore, this method of co-doping will in theory allow for an increase in power factor of the ZnO-based film.

In this study, we have deposited indium co-doped AZO thin films by RF sputtering. Target powers were independently regulated in order to vary film composition. The potential for using this process to control the stoichiometry and film quality has been investigated. Conventionally, sintering has been the primary technique for manufacturing bulk TE metal oxides [8], yet in comparison sputtering is a relatively clean technique which has the capability for nano-scale fabrication of devices. Prepared films have resulted in several interesting relationships between In doping levels, microstructures, and thermoelectric power factors. Also investigated was the thermal stability for each film over a high-temperature operation range.

## 2. Experimental procedure

### 2.1. Film deposition

The samples being investigated in this study are In co-doped AZO films by means of a custom designed stainless steel physical vapor deposition (PVD) reactor equipped with two confocal magnetron sputtering guns. The guns were driven independently by 13.56 MHz rf power supplies. The targets were 3″ diameter disks of $(ZnO)_{.97}(Al_2O_3)_{.03}$ (99.99% purity, Plasmaterials Inc.) and In (99.99% purity, Plasmaterials Inc.). The reactor was evacuated using a combination of a mechanical pump and a turbomolecular pump to a base pressure of $<3 \times 10^{-7}$ Torr. An initial study was performed on the deposition of the solely AZO in order to obtain the highest quality film in terms of high density, high electrical conductivity, and low roughness. The resulting deposition parameters of 2 mT operating pressure, 100 W AZO target power, and a flow rate of 20 sccm Argon (99.999% purity) were then incorporated into the co-sputtering process. The sputtering power of the In target and corresponding growth rates were identified in order to obtain five 200 nm thick $(ZnO)_{1-x-y}Al_xIn_y$ samples, with varying In concentrations.

Films in this study were simultaneously deposited on both n-type (1 0 0) Si wafer substrates, with a resistivity of 100 Ω cm, and glass substrates. Before deposition, the substrates were ultrasonically cleaned by acetone, isopropyl alcohol, rinsed with DI water, and subsequently dried in flowing nitrogen gas. The substrate temperature during deposition was held constant at 150 °C.

### 2.2. Material characterization

The as-deposited films were characterized in terms of thickness, surface texturing, and composition using scanning electron microscopy (SEM) and Auger electron spectroscopy (AES). Identification of structural phases of the as-deposited films was performed using X-ray diffraction (XRD).

Samples were contacted with thermally evaporated Al for transport measurements. *I–V* measurements were taken in order to assure ohmic contacts. In order to measure the Seebeck coefficient, where $\alpha = \Delta V/\Delta T$, two cylindrical heaters were bored into copper blocks, each having independent temperature controls, resulting in a gradient. Using CuNi/NiCr thermocouples at the electrical contacts and a micro-voltmeter we were able to measure the temperature ($\Delta T$) and voltage ($\Delta V$) differentials across the sample. A more in-depth description of this technique is described elsewhere [9]. Temperature-dependent electrical conductivity measurements were measured by a standard dc four-probe technique.

## 3. Results and discussion

### 3.1. Structural and morphological properties

The RF power dependence of the growth rate and atomic composition of indium (at.% In) are shown in Fig. 1. The growth rate has been calculated from the films cross-sectional thickness measurements, taken with SEM, and its corresponding deposition times. The compositional measurements were taken with a PerkinElmer PHI 600 AES system employing a cylindrical mirror analyzer and a 10 keV primary electron beam. For RF powers between 10 to 20 W we obtain In atomic concentration levels from 2 to 10%. Above this level, films demonstrated poor substrate adhesion presumably because they surpassed the solubility limit of In in the ZnO matrix. It is also important to note that the as-deposited concentration levels remain uniform throughout the film. This is in contrary to previously reported literature, which found that In dopant concentration decreases from surface to substrate, by roughly 2% [10].

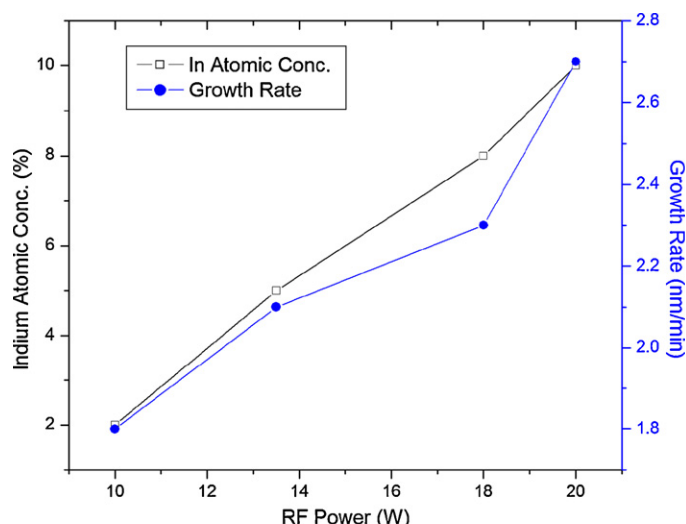


**Fig. 1.** Indium target RF power dependence of % In atomic concentration in AZO film and growth rate.

Phase identification was carried out on a Scintag XRD equipped with a Cu Kα X-ray source and a horizontal wide-angle four-axis goniometer with stepping motors which allowed independent or coupled theta/2-theta axes motion. Precursor films were scanned from 20 to 60°. The collected XRD measurements were compared to reference patterns from the standard Joint Committee for Powder Diffraction Standards (JCPDS) powder diffraction file (PDF). For comparison purposes, all sample data has been normalized to its maximum peak intensity.

As per the XRD spectra in Fig. 2, films with 0 and 2 at.% In have a sole detectable diffraction peak, which is nearly consistent with that of the (0 0 2) standard ZnO crystal plane. For these low concentration In films, (0–2%), the location of the measured diffraction peak does not change significantly, but becomes less intense and broader with the In doping. Using the Debye–Scherrer formula the grain sizes for these two films were found to be 90 and 60 nm, for 0 to 2 at.% In, respectively. This may be due to the large In atomic radius in comparison to that of the Zn. At 5 at.% indium, we obtain the (1 0 0) ZnO peak and further doping results in a transfer of preferred film orientation from the (0 0 2) to this (1 0 0)

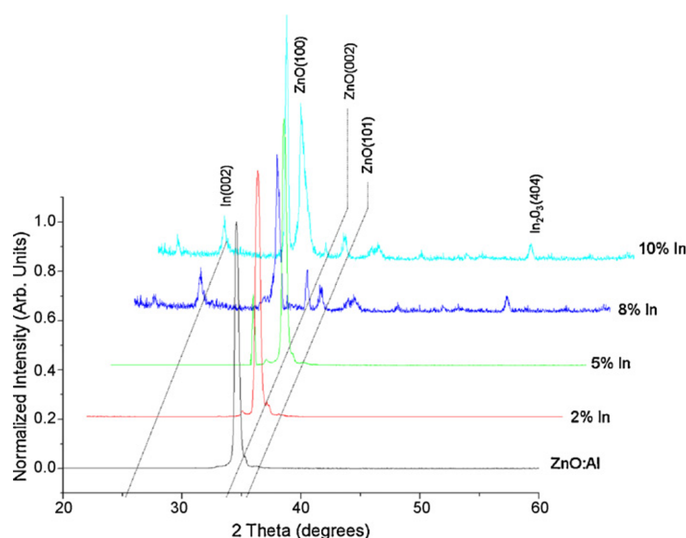


**Fig. 2.** XRD spectra showing that films with 0 and 2 at.% In have a sole ZnO (0 0 2) peak and increased doping results in poly-crystalline growth. At 10% In doping ZnO (1 0 0) becomes the preferred orientation, and In based peaks are also be observed.

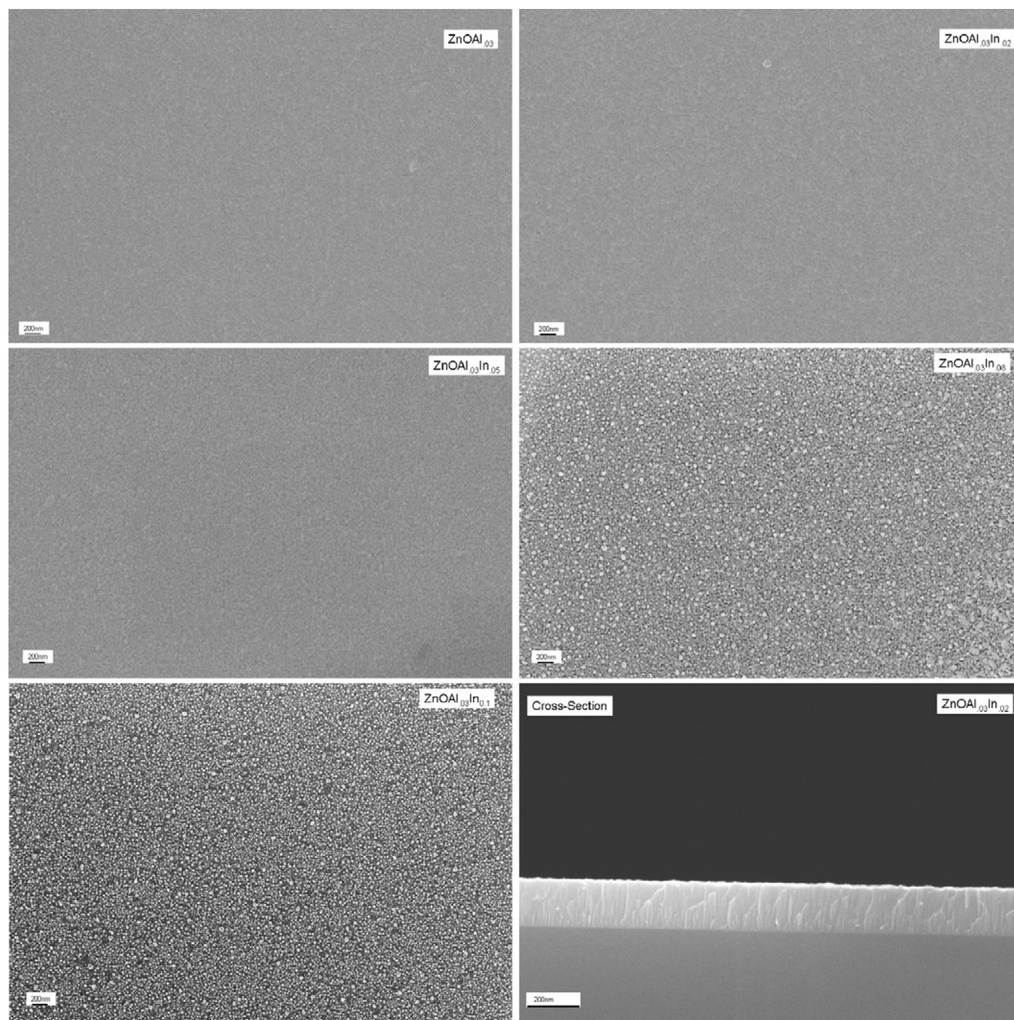


**Fig. 3.** SEM images taken at 10 kV and 100 kX of the as-deposited films. As at.% In increases in the AZO film, grains become more identifiable due to non-uniformity and incoherence. A cross-sectional image is also included to show the columnar growth achieved.

ZnO plane. The 8 and 10 at.% In films are poly-crystalline, which is caused by concentration levels above the In solubility limit resulting in formations of various crystallite orientations. Also, at these concentration levels we observe grains of pure In caused through elemental agglomeration.

Plain-view and cross-sectional morphologies were imaged with a Leo 1550 Schottky source SEM, and are shown in Fig. 3. Images were taken at an accelerating voltage of 10 kV. The film surfaces at 0, 2, and 5 at.% In appear to be smooth and featureless without defects such as crack and protrusions. Further doping results in darker grains and increased granular texture, which is almost certainly due to the In impurity phase. In agreement to the XRD results, the plain-view images show that grain size increases with increased In doping and become less coherent. Individual film thicknesses were found using similar cross-sectional images to the one shown. It is seen that the 2 at.% In film grows with a crystallographically oriented columnar structure. This columnar growth theory for sputtered films was proposed by Thornton [11] and said to occur when deposited at substrate temperatures less than half of the materials melting point temperature (ZnO ~1975 °C).

### 3.2. Thermoelectric measurements

The electrical conductivity ($\sigma$) is determined by $\sigma = Ne\mu$, where $N$ is the carrier concentration, $e$ is the electronic charge, and $\mu$ is the Hall mobility. Based on this equation, we know that we can increase the electrical conductivity in two ways; by increasing the Hall mobility or the carrier concentration. It has previously been shown that in order to increase the mobility we must improve the crystallinity of our films [12]. Our XRD analysis shows highly crystalline AZO films, which leaves little room for improvement. The second option therefore, is to increase the carrier concentration, which can be done via doping.

As shown in Fig. 4a, all films have a similar negative temperature dependence on film $\sigma$ from 300 to 975 K. Films with 0 and 2 at.% In exhibit metallic behavior, with conductivity values of 710 and 1000 S/cm, respectively, at room temperature. Further doping increases the film resistivity by an order of magnitude, for the 5 at.% In film, and 2 order of magnitudes for the 8 and 10% films. This can be attributed to the loss in crystallinity resulting in decreased carrier mobility. This theory was similarly identified in a study of oriented Al-doped ZnO thin films with large crystallite sizes compared to a non-oriented polycrystalline film with the same composition. The results showed a similar dependence on film crystallinity, with the oriented films have an electrical conductivity as high as 2000 S/cm, about five times large than that of the non-oriented film [13].

Theoretically, the Seebeck coefficient, can be solved for by the following equation for an n-type material,

$$\alpha = \frac{-k_B}{e} \ln \frac{N_C}{N_D}, \text{ where } N_C = \frac{2(2\Pi m_C KT)^{3/2}}{h^2} \quad (1)$$

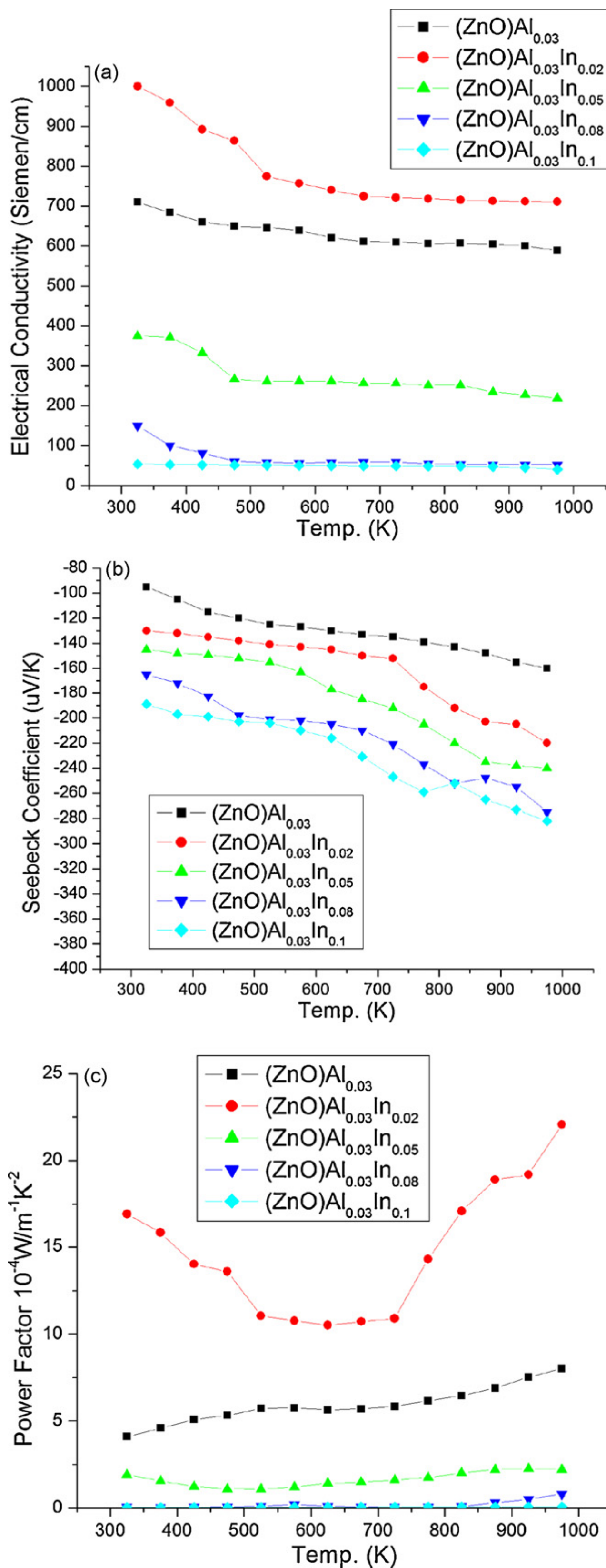


**Fig. 4.** (a) Plot of electrical conductivity as a function of temperature, for AZO and In-doped AZO films. Films with 0 and 2 at.% In achieved values two orders of magnitude higher than 8 and 10 at.% In films. (b) Seebeck coefficient for 200 nm thick AZO films with various doping levels of Indium. A trend of increasing $|\alpha|$ for increased at.% In is observed. (c) Thermoelectric power factors as a function of temperature for In co-doped AZO films with varying doping levels of In.

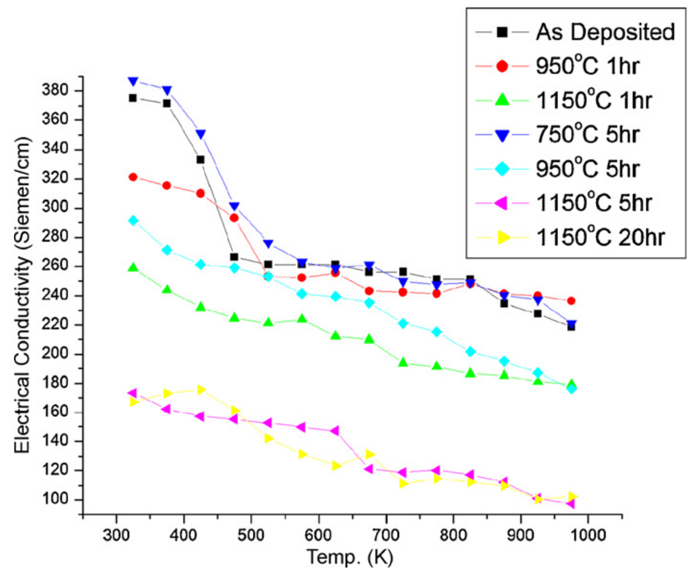


**Fig. 5.** Temperature dependent electrical conductivity for ZnOAl.03In.05 films annealed at 750, 950, and 1150 °C for various time intervals. A significant decline in conductivity is observed for the annealings at 1150 °C for 5 and 20 h, for which AES results show a ±1 at.% In diffusion gradient across the film.

which is derived from the aforementioned equation; $\alpha = \Delta V/\Delta T$. Here, $k_B$ is the Boltzman constant, e is the electron charge, $N_C$ is the effective density of states (DOS), and $N_D$ is the doping density. Using the co-doping method we are able to obtain an increase in the effective density of states by strong band restructuring with the ZnO as our majority component and the localized states from Al and In, being the minority components. Through this restructuring, the low level impurities have created subbands near the original band edges. The localized origin of these subbands, results in a heavy effective carrier mass, which gives rise to a sharp DOS different from the host material. However, at a certain doping level, the increase in DOS begins to tail-off and therefore it is important to determine an optimum doping concentration in order to maximize $N_C/N_D$.

The temperature dependence of the Seebeck coefficient is shown in Fig. 4b. The $\alpha$ values of all the samples are negative, indicating n-type flow. A general trend is seen among the samples with $|\alpha|$ increasing from 300 to 975 K, which is in contrary to bulk ZnO films [14]. The $\alpha$ values for the $(ZnO)Al_{03}$ film are between −100 and −200 μV/K, which is comparable to previously reported literature values [6]. It is also important to note that with increased doping we obtain a nearly proportional increase in $|\alpha|$.

The thermoelectric power factor represents the electrical contribution to the thermoelectric performance. We have calculated it from the electrical resistivity and Seebeck coefficient measurements in Fig. 5a and b, and have plotted the temperature dependence of the power factor for each sample of varying In content in Fig. 4c. For the $(ZnO)Al_{03}$ sample we see that the power factor increases with increasing temperature, owing to the increase in $|\alpha|$. The power factor for this sample is from 4 to $8 \times 10^{-4}\,Wm^{-1}\,K^{-2}$ over the temperature range of 300 to 975 K. These calculated values are lower than the previously reported using a sintering technique [9], which can be attributed to samples size. At 2 at.% In, a large increase in power factor occurs is observed due to its high conductivity and increased Seebeck coefficient. This film unlike all others shows an initial decline, which is then followed by a sharp increase starting at 700 K, ultimately resulting in a large power factor of $22 \times 10^{-4}\,Wm^{-1}\,K^{-2}$ at 975 K, which is three times greater the sample with no In doping. However, although films with greater than 2 at.% In have a continually increasing $|\alpha|$, the degradation in electrical conductivity,

due to the loss in crystallinity, results in significantly lower power factors.

### 3.3. Thermal stability

The stability against increased temperatures for TE materials is an important issue in determining optimum operating conditions and lifetime calculations. A primary concern with the use of In-doping is high temperature diffusion. It has previously been shown through density functional theory calculations, that Zn self diffusion occurs via a vacancy mechanism under n-type condition [15]. This work was based on an indium ion-implanted diffusion study with secondary ion mass spectroscopy (SIMS) analysis, which allows detection of concentration levels at $10^{16}/cm^3$. The results from this study indicated maximum diffusion depths of 0.7 and 1.3 μm at 750 and 850 °C, respectively.

For this study, multiple $ZnOAl_{.03}In_{.05}$ samples were annealed up to 1150 °C for 1, 5, and 20 h time durations in Ar ambient. This film stoichiometry was chosen in order to allow for an adequate amount of In incorporation for identifiable diffusion, as well as having a similar microstructure to that of the 0 and 2 at.% In films. Post-annealing compositions were again determined by AES, using the same sputter rate and power. Films annealed at 750 and 950 °C show only slight diffusion (±0.15%) even after 5 h of annealing. At the annealing temperature of 1150 °C more significant diffusion is observed. At this temperature the 5 and 20 h anneals appears similar, meaning that diffusion has subsided due to reaching a point of equilibrium from the release of stress. At this point of maximum diffusion we see a compositional change of ±1 at.% In, or a 20% variance, across the film. All annealed films with a compositional variance show a general trend of increasing % In with increasing film depth. In order to determined the film quality it is important to investigate how these compositional changes affect the material properties. To summarize these diffusion affects, Fig. 5 is a temperature dependent plot of the electrical conductivity of $ZnOAl_{.03}In_{.05}$ films annealed for various temperatures and times. All films were deposited simultaneously, annealed at their corresponding parameters, and allowed to cool to room temperature prior to electrical measurements. As we observe from the plot, the annealing affects that significantly altered the film conductivity occur at temperature levels of 1150 °C, which is in agreement with diffusion measurements. However, a notable difference is also observed for the film annealed at 950 °C for 5 h, where we saw limited diffusion. Hence, a more precise compositional measurement technique such as SIMS may be used in order to gain a greater understanding of the films thermal stability.

## 4. Conclusion

A comparative study of the thermoelectric power factor of In co-doped AZO, by a co-sputtering process, was investigated for In concentration levels between 0 and 10%. The In concentration level strongly influenced the materials microstructure, which inherently impacted its thermopower. The power factor achieved by doping $(ZnO)Al_{.03}$ with 2 at.% In is roughly three times greater than that with no In doping. However, doping levels >2% led to the formation of poly-crystalline films, which resulted in poor electrical conductivity and thus low power factors. To sum up, it is necessary to have precise control over In doping levels in AZO thin films in order obtain the targeted film microstructure and achieve promising thermoelectric power factors.

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