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Surfaces, Interfaces, and Applications

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Enhanced Thermoelectric Transport and Stability in Atomic Layer Deposited HfO₂/ZnO and TiO₂/ZnO Sandwiched Multilayer Thin Films

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Abstract

Herein, enhancements in thermoelectric performance, both power factor and thermal stability, are exhibited by sandwiching HfO₂ and TiO₂ layers onto atomic layer deposited ZnO thin films. High temperature thermoelectric measurements from 300 to 450 K revealed an almost two-fold improvement in electrical conductivity for TiO₂/ZnO (TZO) samples, primarily owing to increase in carrier concentration by Ti doping. On the other hand, HfO₂/ZnO (HZO) achieved the highest power factor values owing to maintaining Seebeck coefficients comparable to pure ZnO. HZO also exhibited excellent stability after multiple thermal cycles, which has not been previously observed for pure or doped ZnO thin films. Such improvement in both thermoelectric properties and thermal stability of HZO can be attributed to a shift in crystalline orientation from a-axis to c-axis, as well as the high bond dissociation energy of Hf–O, stabilizing the ZnO structure. These unique properties exhibited by ALD HZO and TZO thin films pave the way for next generation transparent thermoelectric devices.

Keywords: Hf-doped ZnO, Ti-doped ZnO, atomic layer deposition, thermoelectric, power factor

1. Introduction

Energy harvesting via the thermoelectric (TE) effect has recently gained attention for its directly reversible heat to electricity conversion [1-5]. Thermoelectric efficiency is described by a dimensionless figure of merit, following the equation: $zT = \sigma S^2 T/\kappa$, where σ stands for electrical conductivity, S for Seebeck coefficient and κ for thermal conductivity [1]. Based on this equation, high performance can be achieved with the combination of high thermoelectric power factor (PF=S² σ) and low κ . However, thermal and electrical conductivity effects are often coupled to each other, challenging the pursuit of high thermoelectric zT. Therefore, studies are currently focused on optimizing the zT by structural engineering, for example by forming nanostructures or superlattice thin films, or by tuning carrier concentration via affecting the internal defects or external doping [2-5].

Among potential thermoelectric materials, oxides are currently being intensively studied owing to their good chemical and thermal stability, low toxicity, high abundance and excellent transparency. Zinc oxide (ZnO) is one of the most studied n-type transparent semiconductor oxides, as its electronic properties can easily be tuned by controlling the defect densities [3-9]. ZnO thin films can be deposited by a wide variety of fabrication techniques, such as atomic layer deposition [10-15], pulsed laser deposition [16], sputtering [17] and solution-based processes [18-19]. However, when doped ZnO thin films are desired, it would be best to conduct both the deposition and doping in a single step to minimize cost, exposure to contamination, processing time and effort. Considering these, atomic layer deposition (ALD) is the ideal technique, as deposition and doping can be conducted simultaneously by simply varying the precursors being pulsed. It is a type of chemical vapor deposition that occurs via sequential, self-limiting surface reactions, precisely growing the materials layer by layer [10-14]. ALD has been gaining interest owing to its excellent control over film thickness and uniformity down to the Ångstrom scale. In addition, ALD allows high controllability over the amount and distribution of dopants. One disadvantage of pure ALD ZnO, though, is its low electrical stability at high temperatures [20-21]. While this could be overcome by the incorporation of other elements, thermoelectric devices based on doped ALD ZnO thin films have been mainly limited to Al and Ga

 [7, 11, 22-24]. Although Al has been a well-established dopant, ALD Al-doped ZnO (AZO) has been reported to exhibit low doping efficiency of only about 13 % [19]. Additionally, group III elements have relatively low stability when doped in ZnO owing to the low electronegativity difference with O [25]. Therefore, alternative dopants should be explored which can simultaneously improve thermoelectric properties and electrical stability.

Group IV elements (Ti, Hf, Zr, etc.) are expected to cause electrical stability when doped to ZnO due to higher electronegativity and weaker ionic character compared to group III elements (Al, Ga, In) [17]. However, these still remain rarely explored as dopants for thermoelectric applications of ZnO. Hf was previously reported to suppress the formation of oxygen vacancies consequently increasing electrical stability [26-28]. Ti, on the other hand, was described to have a higher doping efficiency compared to the more commonly used Al [19]. Several reports have established significant improvements in the electrical properties of both Ti and Hf-doped ZnO, but very few are focused on discussions about its thermoelectric properties. In these few reports, the power factors are still rather low (<10⁻³ mW/mK) [29-31]. Moreover, none of these previous reports on thermoelectric Ti-doped ZnO explored atomic layer deposition.

In this work, the thermoelectric properties of ZnO thin films deposited by atomic layer deposition are tailored by incorporating HfO_2 and TiO_2 layers during deposition. The effect of dopant selection, whether Hf or Ti, in terms of thermal transport and stability of ALD ZnO is also discussed in detail. In addition, the amounts of dopant concentration were optimized to achieve the most desirable thermoelectric power factor.

2. Experimental Section

2.1 Thin Film Deposition and Sample Preparation

Atomic layer deposition of pure ZnO, Hf-ZnO (HZO) and Ti-ZnO (TZO) was performed on precleaned glass and Si (100) substrates using BENEQ TFS-500 ALD reactor. Growth of ZnO was performed at 170°C by sequential pulsing of diethylzinc (DEZn) and H₂O, while in the case of the HZO and TZO, the precursors used were tetrakis(dimethylamido)hafnium(IV) (TDMAHf) or TiCl₄ and H₂O. The TDMAHf solid source was heated to 50°C prior to deposition. Nitrogen was used as the carrier gas, and the deposition pressure was 6.4 Pa. The precursor pulse times are as follows. For ZnO layers, the pulsing sequence used was DeZn (300 ms) - N₂ purge (1s) - H₂O (300 ms) - N₂ purge (1s). The HfO2 pulsing sequence was TDMAHf (1000 ms) - N₂ purge (1 s) - H₂O (250 ms) – N₂ purge (1 s), while that of the TiO₂ layer was TiCl₄ (200 ms) – N₂ purge (1s) - H₂O (150 ms) – N₂ purge (1 s). Three ZnO-HfO₂/TiO₂ supercycles were deposited, wherein one supercycle contains about 0, 1, 2, 3 or 4% Hf or Ti relative to the intended thin film thickness as shown in Fig. 1a. This nomenclature, which pertains to the nominal dopant amount in terms of number of cycles instead of the actual atomic composition, will be used to refer to the samples hereafter.

2.2 Thermal Transport Properties

The samples were diced into 2 cm × 0.4 cm rectangles. Electrode contacts (30-nm-thick Ti/ 40-nm-thick Au) were deposited using electron beam evaporation following the typical four-point probe configuration. Electrical conductivity and Seebeck coefficient measurements were performed for one cycle, from 300 to 450 K (heating stage) and back (cooling stage) using Linseis LSR-3 under He environment. Thermoelectric properties at low temperature were also obtained using a physical properties measurement system (PPMS, Quantum Evercool II) from 100–300 K under vacuum (~1Pa). Carrier concentration and hall mobility were measured at RT using Ecopia HMS-5300 Hall-effect measurement system following the van der Pauw technique [32].

2.2 Characterization

The structural properties of the pure and doped ZnO samples were characterized by asymmetric grazing incidence X-ray diffraction (GIXRD, 0.35 deg. omega angle of incidence) and symmetric X-ray diffraction as well as X-ray reflectivity (XRR) using a Rigaku SmartLab diffractometer equipped with a 9 kW rotating Cu anode (0.154 nm), HyPix-3000 single photon counting detector and K α_1 monochromator. X-ray photoelectron spectroscopy (XPS, PHI5000 VersaProbell, ULVAC-PHI) spectra were measured at RT with Al-K α radiation (1486.6 eV) to analyze the chemical properties and bonding states of the thin films. The raw XPS data were analyzed using a commercial software (CasaXPS), wherein the O1s core levels were fitted using GL30 function (70% Gaussian, 30% Lorentzian) after Shirley background subtraction, and full width at half maximum (FWHM) value was 1.4 eV. All XPS spectra were calibrated with respect to the C1s peak (284.8 eV) to account for charging effects. Secondary ion mass spectroscopy (SIMS) analysis was also conducted to observe the Hf/Ti distribution within the ZnO. The cross-sectional thin film morphologies were then imaged using transmission electron microscopy (TEM, JEOL JEM-3100FEF at 300 kV), while topview planar images were obtained using scanning electron microscopy (SEM, Hitachi SU6600) and atomic force microscopy (Shimadzu SPM-9600). The thin film thicknesses were measured via ellipsometry (Plasmos SD 2300).

3. Results and Discussion

3.1. Thin Film Properties

The ALD doping scheme of the thin film samples as shown in Fig. 1a was intentionally designed in a multilayer fashion. The HfO_2 and TiO_2 layers were inserted in between three layers of ZnO, such that about a total of 615 cycles of oxide material was achieved. Additional 5 cycles were deposited for each ZnO layer to promote ZnO renucleation, which may have been disrupted by the insertion of the HfO_2/TiO_2 layers. Ruoho et al. have previously confirmed that this stacking design is more effective in preserving the crystallinity and mobility of the pure ZnO, compared to a more distributed insertion of dopant layers [7].

The distribution of the Hf and Ti on the HZO and TZO films were investigated by measuring the SIMS depth profile, as shown in Fig. 1b and c. The formation of both HfO_2 and TiO_2 layers sandwiched in between ZnO layers can be confirmed from the 180Hf + 16O and 48Ti peaks located at almost every third of the film thickness. The presence of alternately stacked multilayers is also supported by XRR presented in Fig. S1. Fitting parameters used in the XRR analysis are indicated in Table S1.

Thin film properties such as thickness and surface roughness of the samples containing different percentage of dopant concentrations are summarized in Table 1. The film thicknesses were measured by ellipsometry. Also indicated are the expected thickness of a single dopant layer, which was derived from the number of cycles and the total film thickness from ellipsometry. The actual thickness of each dopant layer is challenging to confirm using XRR due to high film roughness (\sim 3–5 nm), as well as the fact that the growth rate per cycle (GPC) of pure TiO₂ and HfO₂ changes when co-deposited. The surface roughness of the thin films obtained from the AFM analysis are also presented. The doped samples revealed significantly lower surface roughness values compared to the pure ZnO thin film. The AFM images for all samples are displayed in Fig. S3. This is advantageous since smoother surfaces are generally more favorable for better charge transport.

HfO₂/TiO₂ layer

(2, 4, 6, 8 cycles)

200-200*n + 5 cycles

n = nominal at. %

(1%, 2%, 3%, 4%)

(203, 201, 199, 197 cycles)

180 Hf + 16 O

300

ZnO

300

glass

48 Ti

400

400

200*n cycles

ZnO layer

🌒 Zn

Hf/Ti

0

(a)

supercycles

(b)10⁶

Intensity (counts) $^{\circ}$ 10 $^{\circ}$ 10

10

(c) 10⁶

Intensity (counts)

10⁵

10⁴

10³

 10^{2}

10¹

ZnO

00

Q

100

200

Sputtering Time (sec)



57

58 59

60

Fig. 1. (a) Doping scheme indicating the position and thicknesses of the HfO_2/TiO_2 layers, (b) SIMS profile of 3%HZO samples ascribed to 180 Hf + 16 O, and (c) SIMS profile of 3%TZO samples ascribed to 48 Ti.

ZnO

200

Sputtering Time (sec)

2
3
4
5
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Samula 7nO		НΖО				TZO			
Sample	Die ZnO	1% Hf	2% Hf	3% Hf	4% Hf	1% Ti	2% Ti	3% Ti	4% Ti
Total Measured Thickness	114.8 ± 0.1	121.1 ± 0.2	120.6 ± 0.5	118.3 ± 0.4	117.1 ± 0.6	116.6 ± 0.2	114.7 ± 0.3	111.6 ± 0.6	114.9 ± 0.2
Expected Single Dopant Layer Thickness	-	0.39	0.78	1.15	1.52	0.38	0.75	1.09	1.49
Ave. Rms	1.55	1.06	1.38	1.04	0.80	1.08	1.26	1.06	1.16

Table 1. Thin film properties of all samples. Thickness (nm) was measured by ellipsometry, whereas root mean square surface roughness RMS (nm) is determined by AFM.

Figures 2a–c present the cross-sectional high resolution TEM (HRTEM) images of the pure ZnO, 3%TZO and 3%HZO samples. A polycrystalline nature can clearly be observed from the HRTEM images and the corresponding nanobeam diffraction (NBD) images (inset). Distinct lattice fringes with thicknesses of 0.28 nm and 0.26 nm are also visible, which can be attributed to the interplanar distances between the (100) planes and the (002) planes of wurtzite ZnO, respectively. The NBD image of the ZnO sample as shown in Fig. 2a reveals bright spots corresponding to both (002) and (100). For the TZO sample, the dominance of the bright ring ascribed to (100) can be noted, while that of (002) is more pronounced for the HZO sample. The surface morphologies of the thin films were also examined using SEM. The pure ZnO sample in Fig. 2d showed granular structures, which became finer and more elongated in the case of TZO (Fig. 2e). Even finer grains were revealed in the case of the HZO sample, as shown in Fig. 2f. These morphological evolutions could be attributed to the presence of the dopant layers. The more pronounced contrast along the grain boundaries for the TZO sample in Fig. 2e likely physically represents the co-existence of TiO₂ and ZnO in the thin film. On the other hand, the HZO sample revealed even finer grains, which could indicate a shift in grain

orientation. This would more clearly be understood in the XRD analysis.

The structural properties of the thin films were evaluated using asymmetric GIXRD and symmetric XRD. Crystalline phases were identified using asymmetric surface sensitive GIXRD scans as shown in Fig. 2g and 2h. The grown films revealed a polycrystalline nature with a ZnO hexagonal wurtzite structure, which corroborated with the TEM-NBD analysis. All visible peaks can be attributed to the standard diffraction pattern of wurtzite ZnO (JCPDS 043-002), which suggests that only minimal Hf or Ti oxide formation occurred compared to ZnO. The peaks correspond to the (100), (002), (101), (102), (110), (103), and (112) planes of wurtzite ZnO. For the TZO samples, all films revealed a dominant (100) orientation, as also seen in symmetric theta/2theta scans (Fig. S2), which is sensitive to planes parallel to substrate. The dominance of the (100) plane is expected for the current deposition temperature of 170°C, as similarly observed in a previous literature [33]. No further peak changes can be observed by varying the percentage of Ti dopant concentration. On the other hand, Hf doping showed a more complex effect on the ZnO lattice. At 1% doping, (002) orientation is slightly degraded but otherwise comparable crystallinity is observed compared to pure ZnO. Similarly, in symmetric scans (Fig. S2), this 1% Hf doping increases the (100) orientation parallel to surface. However, when 2% and more dopants are introduced, the dominance of the (100) is suppressed, preferring the (002) orientation instead. Overall preferred orientation is decreased resulting in comparable intensities of (100), (002) and (101). This is expected since doping often disrupts ZnO crystallinity. Further increasing to 3% led to shifting the dominance to the (002) peak, which corresponds to the ZnO c-axis orientation. The c-axis orientation was sustained even when a 4% doping amount was reached. The preferential (100) orientation is typical for pure ZnO deposited by ALD likely owing to the charge neutrality of the (100) plane, as opposed to the positively-charged polar (002) planes which attract broken ethyl group fragments [27]. The shift in orientation from (100) to (002) in the presence of a minimum of 3% Hf possibly arises from the disturbance of the (100) charge neutrality by the Hf⁴⁺ ions. This leads to favoring the growth orientation towards the plane of least surface energy, which is the (002) plane [27]. This phenomenon could not be observed with TZO possibly since Ti^{4+} ions are significantly smaller than Hf^{4+} , so they could not have been affecting the growth orientation as much.



Fig. 2. Cross-sectional TEM image of (a) ZnO, (b) 3% TZO and (c) 3% HZO samples and their corresponding nanobeam diffraction patterns (inset), top-view SEM images of (d) ZnO, (e) 3% TZO and (f) 3% HZO samples, and XRD spectra of (g) HZO samples and (h) TZO samples of varying the percentage of dopant concentrations.

3.2 Effect of Doping Element on the Thermoelectric Performance

The effect of doping element on the thermoelectric properties (σ , S and PF) was investigated within the range of 300 and 450 K and presented in Fig. 3. The properties are shown for one thermal cycle, comprising a heating stage (300 K to 450 K) and a cooling stage (450 K to 300 K). The doping level for both TZO and HZO used in the measurement were both 3%. For both electrical conductivity and Seebeck coefficient, all samples exhibited instability between the heating and the cooling stage properties. This phenomenon has also been previously observed in ALD ZnO [10]. It was said that ZnO thin films typically need to undergo a first thermal cycle in order to stabilize. Heat exposure likely causes instability in the ZnO via formation of acceptor defects, leading to significantly degraded thermoelectric properties after an initial heating measurement run [10]. Fig. 3a reveals the largest deviation in electrical conductivity for TZO, while the one that exhibited the least instability is HZO. Despite this, the TZO still emerged as the most conductive throughout the temperature range during cooling, followed by the HZO. Pure ZnO evidently suffered from a severe degradation in σ . The instability in Seebeck coefficient was similarly largest with ZnO, while both TZO and HZO exhibited only modest changes. In effect, ZnO displayed the largest decrease in power factor. The PF of the TZO sample showed a small instability, which can mostly be attributed to the large decrease in electrical conductivity. However, almost no instability in PF is observed for HZO, implying that the small deviations in both electrical conductivity and Seebeck coefficient likely compensate each other. Nevertheless, both doped samples outperformed the pure ZnO thin film for all temperatures during the cooling stage. The highest PF values were consistently observed for HZO, with a maximum PF of 0.143 mW/mK² at about 450 K. The highest PF values achieved for TZO and ZnO are 0.123 mW/mK² and 0.104 mW/mK^2 , respectively, also at 450 K.

In order to further understand the nature and extent of the instability, low temperature cyclic thermoelectric performance was evaluated from 100 to 300 K. This was conducted to isolate the effect of heat on the instability. It can be observed from the plot of electrical conductivities in Fig. 3(d) that

even at very low temperature conditions, instability is still imminent in the pure ZnO sample. In the case of TZO, this instability is somehow reduced especially during the second thermal cycle. However, in the presence of Hf, the instability is completely eliminated. Although this has rarely been observed in relation to thermoelectricity, Hf has been previously reported to improve electrical stability of ZnO. According to previous literature, this high electrical stability was attributed to the suppression of oxygen-related defects caused by Hf [27-28]. Oxygen-bond breaking can lead to the formation of interstitial oxygen, an acceptor defect that likely reduces free electron concentration. However, the reason behind the defect suppression has not been sufficiently elaborated in these reports. This can likely be explained by the significantly stronger chemical bonding of Hf–O compared to Zn–O. Table 2 summarizes the bond dissociation energies and electronegativity differences of the bonds under study. The electronegativity difference between Hf and O is significantly higher in comparison to both Ti–O and Zn–O, which probably results in stronger Hf–O bonds. In addition, the bond dissociation energy of Zn–O is only about a fourth that of Hf–O, and about a third that of Ti–O. This implies that once the Hf or Ti substitutes onto Zn vacancy sites to bond with oxygen during deposition, they would require high energy to break. Zn vacancies are regarded as acceptor defects as well, so Hf/Ti substitution can also likely improve free electron concentration. However, the high bond dissociation energy can also suggest that Hf–O bonds are more difficult to form and are likely of lower concentration compared to Ti–O. In any case, the layer-by-layer self-limiting growth by ALD could likely have helped in forming Hf–O bonds even at a relatively low temperature (170°C) compared to other techniques [34-35]. The cyclic measurements for Seebeck coefficients at low T, on the other hand, remained constant for all samples throughout the temperature range, as shown in Fig. S4.



Fig. 3. High temperature thermoelectric properties showing (a) electrical conductivity, (b) Seebeck coefficient, and (c) power factor for HZO, TZO and ZnO from 300 to 450 K. Low T cyclic electrical conductivity measurements for (d) ZnO, (e) TZO and (f) HZO from 100 to 300 K.

Table 2. Bond dissociation energies of Zn, Hf and Ti with O, and ionic radii of each element [36].

	Bond Dissociation Energy (kJ/mol)		Ionic Radius (pm)
Zn–O	<250.0	Zn	74
Hf–O	801.0	Hf	72
Ti–O	666.5	Ti	56

To experimentally confirm the relationship between oxygen-related deficiencies and thermoelectric stability, high resolution surface XPS spectra were obtained before and after the high temperature TE properties measurement. These spectra likely represent both HfO₂/TiO₂ and ZnO layers. XPS surface sensitivity is about a few nanometers (~ 2 nm), while the thickness of the HfO₂ and TiO₂ layers are expected to be about 1.1 nm from the surface, assuming totally no interlayer mixing occurred. Presented in Fig. 4 are the XPS O1s core level peaks of the samples, deconvoluted into three components: M–O_I, M–O_{II} and M–O_{III}, centered at 529.9 \pm 0.1 eV, 531.2 \pm 0.1 eV and 532.0 \pm 0.1 eV, respectively. The M-O₁ peak corresponds to the metal-oxygen lattice bond, which means the O²⁻ ions are attached to three metal atoms. The M-O_{II} peak represents the O²⁻ ions in the oxygen-deficient regions, which can be related to oxygen vacancies. Finally, the surface adsorbed oxygen such as hydroxyl (-OH) and carbonyl (-COOH) are characterized by the M-O_{III} peak [10, 37-39]. Prior to the thermal cycle, ZnO showed the highest M–O₁ among the samples (Fig 4a), which is expected as Zn–O bonding requires the least amount of energy to form compared to Ti-O and Hf-O [36]. In effect, ZnO displayed the lowest M–O_{II} peak percentage. The high probability to form Zn–O bonds due to low bond formation energy likely leads to fewer oxygen-deficient defects. In the case of TZO and HZO, stronger M–O_{II} peaks are observed. Extrinsic Ti^{4+} and Hf^{4+} ions from the precursors tend to attract oxygen from the ZnO matrix during the free competitive growth of Ti-O/Hf-O and Zn-O, and simultaneously form oxygen vacancies during the process [19, 40]. After the thermal cycle, significant changes in the M-O_{II} peaks can be observed. For the pure ZnO thin film in Fig. 4d, the amount of M–O_{II} spiked from 4.7% to 26.0%, which is expected as heating may easily cause Zn–O bond-breaking. Oxygen atoms tend to be diffused out in the low pressure, oxygen-deficient He environment during the thermal cycle [41]. TZO, on the other hand, showed only a slight increase in M–O_{II}, from 15.1% to 20.9%. With this, it could be said that the strength of Ti-O bonds could somehow be slightly suppressing the formation of oxygen vacancies. This could arise from the almost twice the bond

dissociation energy of Ti–O compared to Zn–O. However, when Hf is added, the amount of $M-O_{II}$ decreased slightly. While a huge amount of bond-breaking could have occurred in pure ZnO during the thermal cycle, HZO seemed to have withstood this, similarly owing to the high bond dissociation energy of Hf–O. This supports the previous hypothesis that the oxygen-related defects are being suppressed when ZnO is doped with Hf. Thus, HZO appears to be more electrically stable than both TZO and pure ZnO.



Fig. 4. XPS O1s deconvoluted peaks before the thermal cycle for (a) ZnO, (b) HZO and (c) TZO, and after the thermal cycle for (d) ZnO, (e) TZO (3%) and (f) HZO (3%).

3.3 Effect of Nominal Percentage of Dopant Concentration

To confirm the effect of dopant concentration on the charge transport properties, Hall effect measurements were performed at RT on the as-deposited samples prior to applying any heat cycle.

Shown in Fig. 5 are the plots of carrier concentration and Hall mobility (μ) vs. dopant concentration. The carrier concentration (n) initially gave negative values, which indicate typical n-type semiconductor behavior, but are presented here in absolute value for simplicity. Doping with Ti resulted in a significantly higher carrier concentration compared to the pure ZnO thin film, leading to high electrical conductivity even at 1% doping concentration. On the other hand, the addition of Hf did not appear to result in successful doping. Minimal changes in both n and μ were observed regardless of the doping concentration. As the carrier concentration could also be affected by intrinsic defects such as oxygen vacancies, the lower carrier concentration of Hf suppresses the formation of such vacancies.



Fig. 5. Hall effect measurements showing (a) carrier concentration and (b) mobility of all samples.

As discussed earlier, the cooling stage values represent more reliably the TE properties of the samples. Because of this, the effect of the amount of dopants in the cooling stage thermoelectric properties (from 450 K to 330 K) is examined and the plots are displayed in Fig. 6. Among the TZO samples, 1% TZO exhibits the highest electrical conductivity, and there is a decreasing trend for electrical conductivity with amount of Ti. This is in contrast with the Hall measurements, which were taken before any thermal cycle, where the 3% TZO exhibited the highest mobility and carrier

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concentration. This means that excess Ti⁴⁺ could have reduced the electrical conductivity upon stabilizing after a thermal cycle. Nevertheless, even only a small amount of Ti could lead to an almost five-fold increase in electrical conductivity. On the other hand, the Seebeck coefficients of TZO were evidently lower than pure ZnO and display only small changes with dopant % concentration. This implies that the Ti is more likely to cause minor structural changes to ZnO, as seen by the direct effect on the electrical conductivity but minimal influence on Seebeck coefficient. Highest PF, therefore, was observed for 1% TZO with a value of 0.136 mW/mK². Adding Hf, on the other hand, results in a slightly different behavior. Improvement in electrical conductivity was observed only from 3% Hf, which incidentally is where the change in thin film crystal orientation was observed to occur, as revealed by the XRD analysis. This suggests that c-axis i.e. (002) aligned HZO leads to improved electrical conductivity, probably owing to the shorter electron path length along the c-plane, as well as diminished grain boundary scattering between grains similarly aligned along the c-axis, as previously reported for c-axis aligned ZnO thin films [39, 41-44]. Also, this could have arisen from free electron generation caused by substitution of Hf⁴⁺ onto Zn²⁺ sites. The value for 2% Hf was not included as the resistivity was higher than the equipment limit probably due to misfabrication. Seebeck coefficients, on the other hand, were slightly smaller for HZO compared to ZnO throughout the temperature range, but were not as low as those of TZO. Unlike in TZO, the non-drastic electrical conductivity improvement for HZO naturally led to minimal decrease in Seebeck coefficient. The combination of a relatively high Seebeck coefficient and decent electrical conductivity led to an almost two-fold improvement in PF for 3% and 4% HZO compared to ZnO. The highest PF was obtained at 450 K for 3 % HZO at 0.157 mW/mK². Nonetheless, incorporation of Ti or Hf dopants both enhanced the thermoelectric PF of ZnO during the cooling stage. In the case of TZO, even only 1% doping can significantly enhance the PF of ZnO, while 3% HZO resulted to highest PF for all doped samples.

In this paper, both Hf and Ti exhibited their individual merits as dopants for ALD ZnO thermoelectric thin films. Therefore, it is possible that both stability and improved thermoelectric

power factor can be achieved when Hf and Ti are co-doped in ZnO. In addition, since Hf is a relatively rare element, using this in conjunction with a high doping efficiency element such as Ti may lead to cheaper, high performance thermoelectric devices.



Fig. 6. High T thermoelectric properties at cooling stage showing (a) electrical conductivity, (b) Seebeck coefficient, and (c) power factor for TZO, and (d) electrical conductivity, (e) Seebeck coefficient and (f) power factor for HZO, from 450 to 300 K.

4. Conclusion

In summary, HfO_2 and TiO_2 layers were infused into ALD ZnO thin films to enhance their thermoelectric performance. Sandwiching TiO_2 layers in between ZnO layers during ALD doubles the carrier concentration compared to pure ZnO, leading to an enhanced thermoelectric power factor. Meanwhile, incorporating HfO_2 to form HZO thin films led to a significant improvement in thermal stability owing to the film orientation shifting and strong Hf-O bonding. The Seebeck coefficients of HZO samples were also almost retained to similar values with ZnO, which led to achieving the highest thermoelectric power factor among all samples. Optimizing the nominal percentage of dopant concentration for all samples resulted in obtaining the highest power factor at 1% for TZO and 3% for HZO, with values of 0.136 mW/mK² and 0.143 mW/mK², respectively.

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Supporting Information

XRR analysis showing experimental (red) and fitted (blue) spectra for all samples, fitting parameters used in XRR analysis, symmetric theta/2theta XRD patterns, AFM images of HZO and TZO samples with their corresponding RMS values, cyclic Seebeck coefficient measurements.

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