Electron scattering mechanisms in polycrystalline sputtered zinc tin oxynitride thin films

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ABSTRACT

Zinc tin nitride (ZnSnN_2) is an emerging ternary nitride semiconductor studied for applications in solar cells, light-emitting diodes, and other optoelectronic devices. For all of these applications, the charge carrier mobility is an important property. However, the dominant electron scattering mechanisms in ZnSnN_2 are unclear, especially in the presence of oxygen that is often incorporated during thin film sputter deposition of this material. In addition, there are no experimental reports on the concentration of defects in such polycrystalline sputtered zinc tin oxynitride $\text{Zn}_{1+x}\text{Sn}_{1-x}\text{N}_{2-2x}\text{O}_{2x}$ (ZTNO) thin films. Here, we address both of these questions using temperature-dependent Hall effect measurements of sputtered ZTNO thin films as a function of Zn composition and O content. The measured temperature dependence of the mobility is fitted to scattering on ionized and neutral defects and to grain boundary scattering. The results indicate that ZTNO is a heavily compensated semiconductor, with a high density of neutral defects dominating the electron scattering processes. First principles theoretical calculations indicate that these neutral defects are likely to originate from the abundant $\text{Zn}_{\text{Sn}}-2\text{O}_{\text{N}}$ complexes in the ZTNO material. Overall, these results establish the dominant electron scattering mechanisms in polycrystalline sputtered ZTNO and help position this material for future use in optoelectronic devices.

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I. INTRODUCTION

Zinc tin nitride (ZnSnN_2) is an emerging ternary nitride semiconductor that crystallizes in a wurtzite-derived structure with different degrees of order on the cation sublattice. It has been considered as a promising photovoltaic solar absorber material due to the Earth-abundance of its elements and its tunable direct bandgap of 1.0–2.0 eV.¹ In addition, ZnSnN_2 has also been studied as a candidate material for light-emitting diodes (LEDs)² and other important applications.³ Specifically, sputtered ZnSnN_2 is the subject of ongoing active research.^{4–6} While early ZnSnN_2 thin film studies for these applications reported on degenerate electron concentration indicated by free carrier absorption and a Burstein-Moss shift of the optical absorption onset, several methods have been recently developed to tackle this issue. For example, carrier concentration can be controlled by increasing the $\text{Zn}/(\text{Zn} + \text{Sn})$ ratio above

stoichiometry⁷ and by growing films with added hydrogen and subsequently annealing.⁸

The defect physics model that has been proposed in the literature to explain the aforementioned electron density observations in ZnSnN_2 is as follows:⁸ (1) stoichiometric ZnSnN_2 is degenerately n-type doped due to spontaneous formation of intrinsic and extrinsic donors during growth, such as O_{N} , V_{N} , and Sn_{Zn} ; (2) depositing Zn-rich off-stoichiometric films introduces Zn_{Sn} acceptor-like defects, thereby decreasing the electron concentration; (3) the presence of hydrogen passivates the Zn_{Sn} acceptors during growth, increasing their solubility and decreasing the driving force for donor defect formation; and (4) the hydrogen is driven out during annealing, freeing up the Zn_{Sn} acceptors to lower the carrier concentration upon activation. In addition to decreasing the electron concentration, increasing Zn content in the film has had a positive effect on

charge carrier mobility, increasing it from $\mu \leq 1 \text{ cm}^2/\text{V} \cdot \text{s}$ for stoichiometric films to $\mu > 5 \text{ cm}^2/\text{V} \cdot \text{s}$ for Zn-rich films.⁷ It has been proposed that the complexing of defects as the films become increasingly Zn-rich is the basis for this increase in mobility.⁷

More recent experimental⁹ and computational¹⁰ reports highlight the importance of oxygen incorporation in the ZnSnN_2 films in determining these electronic properties. For example, near band edge photoluminescence from well-resolved excitons and shallow defects has been recently reported, despite the substantial amount of oxygen $[\text{O}/(\text{O} + \text{N}) = 0.28]$ in Zn-rich $[\text{Zn}/(\text{Zn} + \text{Sn}) = 0.67]$ ZnSnN_2 films.⁹ To explain these exciting and surprising results, a theoretical model has been developed, including the effects of non-equilibrium synthesis; dopants, defects, and complexes; and the change of the electronic structure with composition and short range order.¹⁰ This model explains that at dilute concentrations in ZnSnN_2 , oxygen acts as an n-type dopant in the form of O_N^+ point defects contributing to the degeneracy of $\text{ZnSnN}_2\text{:O}$ films. However, as oxygen content increases above 2%, the dilute defect model breaks down due to most of the O_N^+ defects being compensated by Zn_Sn defects effectively coupling the O/N and Zn/Sn stoichiometry. Such a material is better viewed as a $\text{ZnSnN}_2/\text{ZnO}$ solid solution, analogous to other II–VI– N_2/ZnO solid solutions studied for various photoelectric applications,¹¹ which can be represented as $\text{Zn}_{1+x}\text{Sn}_{1-x}\text{N}_{2-2x}\text{O}_{2x}$ (ZTNO). It is peculiar that ZTNO enables a lower carrier concentration and near band edge photoluminescence compared to the oxygen-free ZnSnN_2 , despite the higher concentration of oxygen.

The objective of this work is to validate the current understanding of defect physics in polycrystalline sputtered ZTNO thin films. This goal is accomplished by fitting the measured mobility data to electron scattering theory and by comparing the derived defect concentrations with the defects calculated from first principles. First, we gain insight into the relative contribution of each scattering mechanism, finding that neutral defect scattering is the dominant mechanism for the measurement conditions relevant to practical applications. Second, we use this model to derive relevant material properties in ZTNO such as the concentrations of ionized and neutral defects and the grain boundary potential height. By comparing these experimental results with theoretically calculated defects, we find that the measured neutral defect scattering most likely originates from the abundant $\text{Zn}_\text{Sn}-2\text{O}_\text{N}$ defect complex, which is prevalent in Zn-rich O-containing ZTNO thin films. Overall, these research results support the current understanding of defect physics in polycrystalline sputtered ZTNO, highlight the significance of oxygen on the electronic transport properties of the material, and establish a scientific basis for further development of this material for future applications.

II. SCATTERING THEORY

In this work, we compare the experimental mobility data μ_expt obtained from temperature-dependent Hall effect measurements with the theoretical mobility μ modeled for the relevant possible scattering mechanisms: (1) ionized defect scattering due to the high concentration of native defects and those introduced by increasing Zn-richness; (2) neutral defect scattering from the

complexing of oppositely charged ionized defects; and (3) grain boundary scattering due to film polycrystallinity. The total theoretical mobility is calculated from the individual mobilities according to Matthiessen's rule,

$$\frac{1}{\mu} = \frac{1}{\mu_\text{ii}} + \frac{1}{\mu_\text{ni}} + \frac{1}{\mu_\text{gb}}, \quad (1)$$

where μ_ii , μ_ni , and μ_gb are the mobilities due to charge carrier scattering on ionized impurities, neutral impurities, and grain boundaries, respectively.

Ionized impurity scattering is calculated using the Brooks-Herring equation that has been more recently generalized for multiple defects of arbitrary charge state.^{12,13} For the material studied here, with donor defects with charge state $Z = +1$ (O_N , V_N) and acceptor defects with charge state $Z = -2$ (Zn_Sn), the nondegenerate Brooks-Herring equation becomes

$$\mu_\text{ii}(n, T) = \frac{1}{N_\text{D}^+ + 4N_\text{A}^-} \frac{128\sqrt{2}\pi^{1/2}\epsilon^2(k_\text{b}T)^{3/2}}{e^3 m^{*1/2} \left[\ln\{1+y\} - \frac{y}{1+y} \right]}, \quad (2)$$

where N_D^+ and N_A^- are the concentrations of ionized donors and acceptors, ϵ is the static absolute permittivity of the material, k_b is the Boltzmann constant, T is the temperature, e is the elementary charge, m^* is the effective mass of charge carriers, $y(n, T) = 24\epsilon m^*(k_\text{b}T)^2/\hbar^2 e^2 n$, $\hbar$ is the reduced Planck constant, and n is the experimental carrier concentration, related to N_D^+ and N_A^- by $n = N_\text{D}^+ - 2N_\text{A}^-$. For the material studied here, we use the theoretically calculated material parameters $\epsilon = 11.23\epsilon_0$ and $m^* = 0.13m_\text{e}$.¹⁴ A similar equation for the degenerate case is listed in [Appendix A](#).

Scattering due to grain boundaries is modeled as a potential barrier between grains.¹⁵ Depending on the width and height of this potential barrier, current across the grain boundary is dominated by thermionic emission over the grain boundary potential or quantum mechanical tunneling through the barrier.¹⁶ For thermionic emission-dominated current, which is relevant to the nondegenerate case (see [Appendix B](#)), the mobility due to grain boundary scattering is calculated according to the Petritz model¹⁷ refined by Seto¹⁵ given by

$$\mu_\text{gb} = Le \left(\frac{1}{2\pi m^* k_\text{b} T} \right)^{1/2} \exp \left(-\frac{eV_\text{gb}}{k_\text{b} T} \right), \quad (3)$$

where L is the size of the grains and V_gb is the potential height of the grain boundary. A similar equation for the tunneling dominated current, relevant to the degenerate case, is listed in [Appendix B](#).

Neutral impurity scattering is calculated using Erginsoy's analogy of electron scattering by atomic hydrogen.^{18,19} This results in a temperature-independent mobility,

$$\mu_\text{ni} = \frac{1}{N_\text{ni}} \frac{e^3 m^*}{80\pi\epsilon\hbar^3}, \quad (4)$$

for a concentration N_ni of neutral impurities.

III. METHODS

ZTNO thin films were deposited by Radio Frequency (RF) magnetron combinatorial sputtering on Corning EAGLE XG glass substrates at a temperature of 200 °C, using Zn and Sn high purity metal targets. Prior to the deposition, the chamber was evacuated to a base pressure of $<10^{-6}$ Torr. The deposition pressure was 20 mTorr, attained by introducing a mixture of Ar and forming gas (5% H₂, 95% N₂), each at a flux rate of 10 sccm. Directly after deposition, samples were annealed at 400 °C for 6 h under an Ar/N₂ atmosphere (annealing pressure 20 mTorr, gas flux 10 sccm each) before breaking vacuum. A more detailed description of the deposition conditions is reported by Fioretti *et al.*^{7,8}

The resulting thin films were characterized for cation composition using x-ray fluorescence (XRF), for anion composition using secondary ion mass spectrometry (SIMS) calibrated by Rutherford Backscattering Spectrometry (RBS),⁹ and for structure/crystallinity using x-ray diffraction (XRD). The Scherrer equation was used to infer the size of the coherent diffraction domains from the broadening of the XRD peaks. The most intense reflection was used, which corresponds to the (201 or 121) plane, as indexed by Quayle *et al.*² The thicknesses of the samples were estimated from a combination of XRF and profilometry measurements to be 300–600 nm.

Temperature-dependent Hall effect measurements of the ZTNO samples contacted with indium were performed on a Lakeshore CRX-VF probe station with an 8425 Hall measurement upgrade. For accurate Hall effect measurements in the Van der Pauw configuration, ZTNO samples were deposited through a cloverleaf shadow mask. For low mobility samples, measurements were taken at multiple excitation currents, each using the standard current and field reversal to subtract out parasitic voltages. A line was then fit to V_H vs $|I| \cdot |B|$ to extract the Hall constant, where V_H is the Hall voltage, $|I|$ is the magnitude of the current, and $|B|$ is the magnitude of the magnetic field. Grain sizes, needed for the grain boundary mobility analysis, were assumed to be 50 nm based on our previous work (30–70 nm for a range of deposition conditions and Zn concentrations).⁷ The mobility calculations were insensitive to assuming grain sizes between 20 and 70 nm.

Defect formation and pair binding energies were calculated from first principles calculations with the Vienna *Ab Initio* Simulation Package (VASP) using the projector-augmented-wave (PAW) potentials.²⁰ Density functional theory (DFT) with generalized gradient approximation²¹ and on-site Coulomb interactions ($U = 6$ eV) for Zn-d orbitals were employed.²² A $2 \times 2 \times 2$ supercell (Pna2₁, space group 33) with 128 atoms was constructed for defect and defect pair calculations. Defect formation energies with bandgap corrections were performed,²³ where the GW corrected bandgap value ($E_g = 1.41$ eV) was used (<https://materials.nrel.gov>).

Defect equilibrium, by accounting for both defect and defect pair binding, was obtained by solving the self-consistent equation by forcing the charge neutrality between free carriers and charged defects.^{10,24,25} Since the carrier concentration depends on the relative distance of Fermi level to the band edges, oxygen induced band edge shifts were also included in the defect equilibrium simulation.¹⁰ At $T = 700$ K, the defect equilibrium calculation was conducted as a function of oxygen content under Zn-rich conditions (Zn₃N₂ limit). Two defect pairs, $(Zn_{Sn}-O_N)^-$ and $(Zn_{Sn}-2O_N)^0$, play important

roles with the pair binding energies about -0.97 eV and -1.73 eV, respectively, relative to the isolated Zn_{Sn}^{2-} and O_N^+ defects.¹⁰

IV. RESULTS AND DISCUSSION

A. Experimental results

The XRD measurements for the ZTNO films reported in this paper as a function of Zn content determined from XRF (Fig. 1) confirm that they are polycrystalline, single-phase films. This is corroborated by our previous work describing the growth of high oxygen, single-phase ZTNO with homogeneously distributed Zn, Sn, N, and O.^{7,8} In Fig. S1 of the [supplementary material](#), reproduced from our previous work,⁸ cross-sectional scanning transmission electron microscopy (STEM) with energy dispersive x-ray spectroscopy (EDS) is used for a representative sample of ZTNO with $Zn/(Zn + Sn) = 0.64$. The results confirm the phase purity of the material and the absence of precipitates, and their associated electronic effects,^{26,27} at grain boundaries. Although oxygen composition is not shown in the figure, the homogeneous distribution of all other elements of the oxynitride implies the same homogeneity for the distribution of O within the accuracy of the STEM/EDS method, due to the overall charge balance in this semiconducting material.

The XRD patterns change as the films become Zn-rich as both the peaks at $\approx 31^\circ$ and $\approx 46^\circ$ decrease and a peak at $\approx 32.5^\circ$ increases in intensity. In addition, the overall XRD pattern intensity decreases with increasing Zn concentration. This relative peak intensity change may be due to a combination of a changing preferential orientation of the thin films and a changing scattering factor of the smaller Zn atom compared to the larger Sn atom. The overall decrease in intensity may be associated with this same change in the

FIG. 1. XRD patterns of ZTNO samples as a function of Zn concentration measured by XRF, confirming the formation of a single-phase polycrystalline film. As Zn richness increases, the change in relative peak intensity suggests the change in preferential orientation. Decreases of XRD intensity may be in part due to the Zn/Sn scattering intensity difference.

scattering factor in addition to a decrease in the crystallinity of the material at these off-stoichiometric compositions. The coherent diffraction domains, calculated from the line broadening of the XRD peaks, were found to be between 20 and 30 nm, generally decreasing in size with increasing Zn concentration.

To evaluate the oxygen concentration in ZTNO thin films as a function of Zn off-stoichiometry, the relative concentration of O and N was measured by SIMS and analyzed as a function of $\text{Zn}/(\text{Zn} + \text{Sn})$ composition measured from XRF. These relative SIMS measurements were converted to absolute $\text{O}/(\text{O} + \text{N})$ concentrations using our previous publication, where $\text{O}/(\text{O} + \text{N}) = 0.28$ was measured by RBS for the sample with $\text{Zn}/(\text{Zn} + \text{Sn}) = 0.65$.⁹ Figure 2 displays an increasing level of oxygen incorporation with increasing Zn richness beyond $\text{Zn}/(\text{Zn} + \text{Sn}) = 0.6$, as obtained by a combination of SIMS and RBS (y-axis) and XRF (x-axis). This good correlation of the Zn and O content supports the importance of oxygen in the defect physics in ZTNO reported earlier.⁹ The high O content proves to have significant effects on the electronic transport properties reported below.

Figure 3 shows the temperature dependence of the resistivity, the carrier concentration, and the mobility for ZTNO samples of varying Zn composition. As shown in Fig. 3(a), all films exhibit a decrease in resistivity with increasing temperature, which is typical semiconductor behavior. The resistivity and the temperature dependence increase as films become increasingly Zn rich, consistent with previous results.⁷ The carrier concentration [Fig. 3(b)] decreases over several orders of magnitude with increasing Zn composition down to $1.1 \times 10^{17} \text{ cm}^{-3}$ at 300 K, explaining the increase in resistivity in agreement with previous results.^{7,8} The temperature dependence of the carrier concentration is fairly flat, suggesting the

FIG. 2. Oxygen composition as a function of Zn composition for ZTNO samples, measured by SIMS for oxygen content and by XRF for Zn content. The oxygen content at $\text{Zn}/(\text{Zn} + \text{Sn}) = 0.65$ was normalized to $\text{O}/(\text{O} + \text{N}) = 0.28$ measured by RBS.⁹ The solid line is the composition obtained from a defect model based on the mutual compensation between zinc (Zn_{Sn} antisites) and oxygen (O_{N}) content.

FIG. 3. Temperature-dependent Hall effect measurements of ZTNO samples with increasing Zn concentration. (a) As a function of increasing Zn, samples show increasing resistivity due to a decrease in carrier concentration. (b) As a function of temperature, carrier concentration shows little dependence, suggesting the presence of only shallow donors and acceptors. (c) The mobility becomes increasingly temperature-dependent as Zn increases, suggesting a move away from degeneracy. Solid mobility lines and markers are experimentally measured points; dashed lines and open markers are fitted mobilities.

presence of only very shallow donors and acceptors. The mobility is temperature independent for the more stoichiometric (degenerate) samples, as shown in Fig. 3(c). With increasing Zn composition, the samples become nondegenerate and the mobility increases and shows a stronger temperature dependence. The stronger temperature dependence of the mobility for the nondegenerate samples explains the observed temperature dependence of the resistivity. These mobility trends saturate close to the limits of Zn composition reported here ($0.54 < \text{Zn} < 0.66$).

B. Mobility analysis

The mobility of the ZTNO samples in Fig. 3(c) was analyzed using models for both ionized impurity and grain boundary scattering. For the Zn-rich samples ($\text{Zn} > 0.60$), the thermionic emission model [Eq. (3)] for grain boundary scattering (exponential dependence on T) was required to fit the data, in addition to the nondegenerate Brooks-Herring [Eq. (2)] model for ionized impurity scattering (power law dependence on T). For the more stoichiometric samples ($\text{Zn} < 0.60$), a degenerate Brooks-Herring equation [Eq. (A5)] was

used to model ionized impurity scattering or tunneling current-dominated model [Eq. (B4)] was used for grain boundary scattering,^{16,28} each of which is temperature-independent. Overall, the positive or flat temperature dependence of the mobility in all studied ZTNO samples rules out the dominance of other scattering mechanisms with a negative temperature dependence in this temperature range, such as phonons.²⁹ For all ZTNO samples reported in Fig. 3(c), neutral impurity scattering [Eq. (4)] was not included to keep the model to the smallest possible number of free parameters.

By fitting the mobility of the nondegenerate ZTNO samples to the temperature-dependent models, we determined the concentration of ionized donors and acceptors and the height of the potential barrier at grain boundaries. These results are displayed in Fig. 4, along with the measured electron concentration [same as in Fig. 3(b)] used as an input to the mobility model. Based on Fig. 4, the total concentration of ionized donors and acceptors is several orders of magnitude above the carrier concentration, meaning this material is highly compensated. This is quite expected based on the large Zn off-stoichiometry and significant oxygen content (Fig. 2). However, both N_A and N_D decrease with increasing Zn composition. This is unexpected because the concentration of Zn_{Sn} acceptors and O_N donors should increase with increasing oxygen and zinc concentration. The reason for this apparent trend remains unknown, but it may be related to the formation of neutral defect complexes not being taken into account in this model. The grain boundary potentials V_{gb} were fitted to be 0.1 ± 0.04 V, with no significant variation over the Zn composition range.

The results of the mobility analysis for the degenerate ZTNO samples are summarized in Table I. Because for degenerate semiconductors both ionized impurity and grain boundary scattering mechanisms are temperature independent, it is not possible to separate

FIG. 4. Concentrations of ionized donors N_D^+ and ionized acceptors N_A^- at 300 K vs Zn concentration and the potential barrier V_{gb} between grains for the nondegenerate ZTNO samples, calculated from fitting the modeled mobility to the experimental mobility. The high concentration of the modeled N_D^+ and N_A^- compared to experimental carrier concentration n implies that ZTNO is a highly compensated material. The potential barrier at grain boundaries V_{gb} was found to be approximately constant across the Zn composition range at 0.1 ± 0.04 V.

TABLE I. Concentrations of ionized acceptors, neutral impurities, and the height and width of grain boundaries for the degenerate samples if all scattering is attributed to only a single mechanism.

$Zn/(Zn + Sn)$	N_A^- (cm^{-3})	N_{ni} (cm^{-3})	V_{gb} (V)	l_{gb} (nm)
0.538	3.0×10^{22}	4.0×10^{20}	0.1	3.6
0.587	3.0×10^{22}	8.0×10^{20}	0.1	4.9

their relative contributions in this analysis. Thus, Table I lists the concentration of ionized acceptors (similar concentration for ionized donors in highly compensated samples), neutral impurities [Eq. (4)], and the height and width of the potential barrier between grains at 300 K, if only one of these scattering mechanisms is to account for all scattering.

In modeling the grain boundary scattering by tunneling, it is not possible to dissociate the relative contributions from the height V_{gb} and the width l_{gb} of the grain boundary. However, we note that V_{gb} was found not to vary significantly with composition for the nondegenerate samples and that the calculated mobility was insensitive to this parameter. Therefore, V_{gb} was set to a reasonable value of 0.1 V and l_{gb} was found to vary between 3.6 and 4.9 nm (Table I). These results for ZTNO are higher compared to those for

FIG. 5. Temperature-dependent Hall data for a selected nondegenerate ZTNO sample [$Zn/(Zn + Sn) = 0.688$] with higher mobility, allowing quicker measurement of many more data points: (a) measured electron concentration, (b) measured and modeled mobility, and (c) contribution of each of the scattering mechanisms to the inverse mobility.

TABLE II. Summary of the mobility analysis of the experimental data at 300 K for the selected $[\text{Zn}/(\text{Zn} + \text{Sn}) = 0.688]$ sample, including the concentrations of ionized donors, ionized acceptors, and neutral impurities, and the voltage at the grain boundaries, in comparison with the computational data for the concentrations of electrons and defects.

	$\text{Zn}/(\text{Zn} + \text{Sn})$	n (cm^{-3})	N_D^+ (cm^{-3})	N_A^- (cm^{-3})	N_{ni} (cm^{-3})	V_{gb} (V)
Experimental	0.688	1.2×10^{18}	1.0×10^{19}	4.6×10^{18}	1.0×10^{19}	0.03
Computational	0.670	3.76×10^{17}	2.49×10^{19}	2.45×10^{19}	6.23×10^{21}	

Al:ZnO ($l_{\text{gb}} = 0.98 \text{ nm}$),²⁸ as expected since here they account for all scattering.

If only ionized impurity scattering is used to account for all scattering, the analysis yields unphysical values for the concentration of ionized acceptors, given that site density of Zn atoms in ZTNO is only $1.8 \times 10^{22} \text{ cm}^{-3}$ (Table I). So clearly, not all of the scattering can be accounted for by ionized impurities alone. However, when only neutral defect scattering is used to model the mobility of the degenerate samples, the resulting concentration N_{ni} is $4\text{--}8 \times 10^{20} \text{ cm}^{-3}$, which is physically acceptable. This again suggests the importance of the neutral impurity scattering to mobility in ZTNO.

To incorporate the neutral impurity scattering into our mobility model without overdefining the system, a larger number of experimental points were measured for a selected nondegenerate ZTNO sample with $[\text{Zn}/(\text{Zn} + \text{Sn}) = 0.688]$. This sample, displayed in Fig. 5, has a higher mobility, allowing for many more data points to be taken in a reasonable amount of time. The mobility analysis [dashed lines in Fig. 5(b)] has been performed using the nondegenerate Brooks-Herring equation to model ionized-impurity scattering, the thermionic emission current-dominated model for grain boundary scattering, and the Erginsoy model for neutral impurity scattering. The results of the fit are summarized in Table II. It appears that the concentration of all three types of defects (neutral defect complexes, ionized acceptors, and ionized donors) are comparable to each other ($10^{18}\text{--}10^{19} \text{ cm}^{-3}$) and smaller than the concentration of ionized defects in the absence of neutral defects (see Fig. 4 and Table I).

To gain a greater understanding of the relative importance of these three different scattering mechanisms to electron mobility in ZTNO, Fig. 5(c) displays the relative contribution each mechanism has to $1/\mu$, according to Matthiessen's rule [Eq. (1)]. It is apparent from this figure that the majority of scattering is from neutral defects, followed by ionized defects, and lastly by grain boundaries, for these application-relevant nondegenerate ZTNO samples at the operation-relevant room temperature conditions. When the carrier concentration is lowered by lowering the temperature or by increasing Zn composition (not shown), grain boundary scattering takes on an increased proportion of total scattering. This may be related to an increase in the width of the depletion layer (increase in potential barrier width), as the carrier concentration decreases.¹⁵

C. Computational results

The results from the experimental temperature-dependent Hall effect measurements and mobility fitting have pointed to a

highly compensated film with significant scattering by neutral defects, ionized defects, and grain boundaries. To shed more light on the microscopic origin of these observed defect physics in ZTNO, we turn to first principles computational results. The computational methods included the effect of oxygen defects, which proved to be very important in determining the electronic properties of ZTNO.⁹ It also included both single isolated defects, such as the O_N^+ antisite, and complexed defects, such as $(\text{Zn}_{\text{Sn}}-\text{O}_N)^-$, in which an acceptor defect (Zn_{Sn} , $Z = -2$) and a donor defect (O_N , $Z = +1$) are located spatially close to each other such that their Coulombic interaction with charge carriers is modeled as a single defect ($Z = -1$) rather than two separate defects. Other defects included in the computation but found to have negligible concentrations ($N < 10^{15} \text{ cm}^{-3}$) were Zn_{Sn} , Sn_{Zn} , V_N , and all combinations of complexes between donors and acceptors.¹⁰

Computed results for the equilibrium defect concentrations in ZTNO are displayed in Fig. 6 as a function of the $\text{Zn}/(\text{Zn} + \text{Sn})$ ratio, which is linearly proportional to O content as defined by the formula $\text{Zn}_{1+x}\text{Sn}_{1-x}\text{N}_{2-2x}\text{O}_{2x}$ and compared to experimental results in Table II. Several observations are of interest. First, the calculated decreasing trend in the carrier concentration as a function of Zn concentration in ZTNO matches experimental results (compared to

FIG. 6. Concentrations of the most abundant Zn-, Sn-, N-, and O-containing defects in ZTNO, both isolated and complexed, and the carrier concentration n , as calculated from first principles. The significant defects include O_N^+ (singly ionized donor), $(\text{Zn}_{\text{Sn}}-\text{O}_N)^-$ (singly ionized acceptor), and $(\text{Zn}_{\text{Sn}}-2\text{O}_N)^0$ (neutral defect complex).

the measured carrier concentration in Fig. 4) both qualitatively and quantitatively. Second, also consistent with experimental results, ZTNO is a heavily compensated semiconductor with ionized donor and acceptor concentrations much higher than the carrier concentration. Specifically, almost all of the Zn_{Sn} defects are compensated with O_{N} defects—the isolated $\text{Zn}_{\text{Sn}}^{2-}$ are of insignificant concentration. Third, the main donor, acceptor, and neutral defects all exhibit an increasing concentration with Zn richness in ZTNO. Given that all of these defects scatter charge carriers, this would lead to a lower mobility film with increasing Zn concentration, which is contrary to experimental results [see Fig. 3(c)]. One possible explanation for this discrepancy is that the computational results assume full equilibration between isolated and complexed defects in ZTNO. However, this is likely not the case in practice. In particular, it is possible that the degree of complexing is lower at lower concentrations of Zn, leading to a higher concentration of isolated ionized donors and acceptors (and a lower concentration of neutral complexes) than the theoretical calculations predict. This would explain the lower mobility at lower Zn concentrations observed in the experiment. If correct, then it may be possible to increase mobility in the less Zn-rich films by thermal annealing to allow for greater defect pair association, as was observed previously in ZnO.³⁰

V. CONCLUSION

Electron scattering mechanisms in ZTNO thin films have been studied using temperature-dependent Hall effect measurements. These polycrystalline films were prepared by sputtering and had a linearly increasing concentration of oxygen content with increasing Zn content for $\text{Zn}/(\text{Zn} + \text{Sn}) > 0.6$. The results of modeling the electron mobility as a function of measurement temperature and Zn content in the ZTNO films indicate that the dominant scattering mechanism is on neutral defects, with a small effect of ionized impurities at all measurement temperatures and with some contribution from grain boundaries at low temperatures and high Zn concentrations. These neutral defects were assigned to abundant $(\text{Zn}_{\text{Sn}} - 2\text{O}_{\text{N}})^0$ defect complexes using first principles calculations. Other calculated defects have significantly smaller concentrations and do not contribute to scattering. In summary, the results of this work indicate that charge carrier transport in sputtered ZTNO thin films is dominated by defect compensation and support our theoretical model of defect physics in ZTNO.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for the STEM image with EDS composition map of ZTNO, reproduced from our previous work.⁸

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APPENDIX A: IONIZED DEFECT SCATTERING

An ionized defect scatters charge carriers via a shielded coulombic potential of the form

$$\Delta V_{ii} = \frac{Ze^2}{4\pi\epsilon r} e^{-r/\lambda_D}, \quad (\text{A1})$$

where Z is the charge state of the ionized defect, e is the elementary charge, ϵ is the static absolute permittivity of the material, r is the radial distance from the ionized defect, and λ_D is the Debye length. Solving for the mobility results in the Brooks-Herring equation, which is the theoretical upper limit of mobility due to ionized defects of concentration N_i^x , where x is $+$ for donors and $-$ for acceptors in an n-type semiconductor.^{12,31} This equation has been generalized by Look for arbitrary number ionized defects $N_{i,j}^x$ of charge state Z_i by replacing $Z^2 N_i^x$ with¹³

$$\sum_i Z_i^2 N_{i,j}^x. \quad (\text{A2})$$

The Brooks-Herring equation becomes

$$\mu_{ii}(n, T) = \frac{1}{\sum_i Z_i^2 N_{i,j}^x} \frac{128\sqrt{2}\pi^{1/2}\epsilon^2 (k_b T)^{3/2}}{e^3 m^{*1/2} \left[\ln\{1 + y(n, T)\} - \frac{y(n, T)}{1 + y(n, T)} \right]}, \quad (\text{A3})$$

where

$$y(n, T) = \frac{24\epsilon m^* (k_b T)^2}{\hbar^2 e^2 n}. \quad (\text{A4})$$

For a degenerate semiconductor, the equivalent equation is

$$\mu_{ii \text{ degen}}(n) = \frac{n}{\sum_i Z_i^2 N_{i,j}^x} \frac{24\pi^3 \epsilon^2 \hbar^3}{e^3 m^{*2} \left[\ln\{1 + y'(n)\} - \frac{y'(n)}{1 + y'(n)} \right]}, \quad (\text{A5})$$

where

$$y'(n) = \frac{3^{1/3} 4\pi^{8/3} \epsilon \hbar^2 n^{1/3}}{e^2 m^*}. \quad (\text{A6})$$

Here, k_b is the Boltzmann constant, T is the temperature, m^* is the absolute effective mass of the charge carrier, $\hbar$ is the reduced Planck constant, and n is the carrier concentration.

For ZTNO, which is thought to have singly-ionized O_{N} and V_{N} donors ($Z_D = 1$) and doubly-ionized Zn_{Sn} acceptors ($Z_A = 2$), $\sum_i Z_i^2 N_{i,j}^x$ becomes

$$N_D^+ + 4N_A^-. \quad (\text{A7})$$

The validity of the nondegenerate form of the Brooks-Herring equation requires the validity of the Born approximation, which is valid when^{31–33}

$$y(n, T) \gg 1. \quad (\text{A8})$$

For ZTNO, this requires

$$n \ll 10^{14} \text{ T}^2. \quad (\text{A9})$$

APPENDIX B: GRAIN BOUNDARY SCATTERING

Scattering due to grain boundaries is modeled as a potential barrier between grains. This barrier arises from the creation of trapping states due to dangling bonds in the disordered region between two grains which are charged by trapping charge carriers.¹⁵ Depending on the width and height of this potential barrier, current across the grain boundary is dominated by thermionic emission over the grain boundary potential, quantum mechanical tunneling through the barrier, or both. The domination of one of these mechanisms over the other can be attained by calculating the parameter¹⁶

$$E_{00} = 18.5 \times 10^{-12} \left(\frac{n(\text{cm}^{-3})}{(m^*/m_e)(\epsilon/\epsilon_0)} \right)^{1/2} \text{ eV}. \quad (\text{B1})$$

E_{00} gives information about the dominant type of current across the grain boundary by

$$\frac{k_b T}{E_{00}} \gg 1 \quad \text{thermionic emission}, \quad (\text{B2})$$

$$\frac{k_b T}{E_{00}} \ll 1 \quad \text{tunneling}. \quad (\text{B3})$$

For tunneling-dominated current, the mobility is calculated according to the model given by Addonizio *et al.*²⁸ for grains of size L and grain boundaries with a rectangular potential of width l_{gb} and height V_{gb} by

$$\mu_{\text{gb tun}} = \frac{Le}{4\pi^2 \hbar^2} \frac{(2m^* e V_{\text{gb}})^{1/2}}{n l_{\text{gb}}} \exp \left(- \frac{2l_{\text{gb}} (2m^* e V_{\text{gb}})^{1/2}}{\hbar} \right). \quad (\text{B4})$$

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