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Carrier scattering mechanisms limiting mobility in hydrogen-doped indium oxide

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Hydrogen-doped indium oxide (IO:H) has recently garnered attention as a high-performance transparent conducting oxide (TCO) and has been incorporated into a wide array of photovoltaic devices due to its high electron mobility ($>100 \text{ cm}^2/\text{V s}$) and transparency ($>90\%$ in the visible range). Here, we demonstrate IO:H thin-films deposited by sputtering with mobilities in the wide range of $10\text{--}100 \text{ cm}^2/\text{V s}$ and carrier densities of $4 \times 10^{18} \text{ cm}^{-3}$ – $4.5 \times 10^{20} \text{ cm}^{-3}$ with a large range of hydrogen incorporation. We use the temperature-dependent Hall mobility from 5 to 300 K to determine the limiting electron scattering mechanisms for each film and identify the temperature ranges over which these remain significant. We find that at high hydrogen concentrations, the grain size is reduced, causing the onset of grain boundary scattering. At lower hydrogen concentrations, a combination of ionized impurity and polar optical phonon scattering limits mobility. We find that the influence of ionized impurity scattering is reduced with the increasing hydrogen content, allowing a maximization of mobility $>100 \text{ cm}^2/\text{V s}$ at moderate hydrogen incorporation amounts prior to the onset of grain boundary scattering. By investigating the parameter space of the hydrogen content, temperature, and grain size, we define the three distinct regions in which the grain boundary, ionized impurity, and polar optical phonon scattering operate in this high mobility TCO. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5033561>

I. INTRODUCTION

In the field of optoelectronics, transparent conducting oxides (TCOs) are vital for information (Liquid Crystal Display and Light Emitting Diode displays) and energy (photovoltaics and electrochromic windows) devices^{1–3} which require the typically mutually exclusive properties of transparency and electrical conductivity. TCOs are degenerate semiconducting materials with a wide bandgap of $\sim 3 \text{ eV}$, giving them transparency in the visible-to-near infrared (nIR) wavelength regions, and doped to carrier densities (N_e) $> 1 \times 10^{20} \text{ cm}^{-3}$, giving them suitable conductivities for use in such optoelectronic devices.⁴ The continued advancement of optoelectronic devices relies on the improved conductivity and transparency of TCOs. The conductivity depends on three parameters

$$\sigma_e = \mu N_e q. \quad (1)$$

N-type TCOs are exclusively discussed in this work, and therefore, σ_e is the conductivity of electrons, μ is the mobility of electrons, N_e is the electron carrier density, and q is the electronic charge. The simplest way to improve σ_e is to increase N_e through further doping, and indeed, the widely used tin-doped indium oxide (ITO) TCO is typically doped to N_e values $> 5 \times 10^{20} \text{ cm}^{-3}$, depending upon the use of the TCO. However, this increase in N_e degrades transparency due to free carrier absorption (FCA), as $\text{FCA} \propto N_e/\mu$. FCA is an optical absorption process where the photon energy is absorbed by an excited carrier in either the conduction or the valence band, causing it to move to a higher energy state within the same band. These N_e values $> 5 \times 10^{20} \text{ cm}^{-3}$ in ITO lead to strong FCA in the nIR range, causing significant current and efficiency losses in optoelectronic devices such as silicon heterojunction (SHJ) solar cells.⁵ Creating TCOs with lower N_e —and hence lower FCA—causes a decrease in conductivity, leading to deteriorated performance in solar devices. μ is therefore the only parameter remaining in Eq. (1) to achieve higher conductivities while circumventing this trade-off between transparency and conductivity.

Compared to ITO, the μ of hydrogenated indium oxide (IO:H) films is greater by a factor of 3–4,^{6,7} allowing improved nIR transparency without decreasing σ . This allows for high performance in a wide range of photovoltaic

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devices, such as Cu(In,Ga)Se₂ solar cells,^{8–10} perovskite solar cells,^{11,12} and SHJ solar cells.^{5,13–15} However, the root cause of improved μ in IO:H is not fully understood and thus motivates this current study.

Previously, several authors have investigated IO:H and surmised that hydrogen suppresses grain boundary scattering (GBS), allowing a maximization of the mobility.^{6,7,16} Some of these authors additionally conclude that since crystallites in their IO:H films are much larger than the carriers' mean free path (grain sizes on the order of 100s of nm, while the mean free path is on the order of 10s of nm), the in-grain properties dominate the film, and crystallization by annealing improves in-grain properties.⁶ One of those in-grain properties is scattering of free carriers from the ionized impurities which provide the free carriers, which has long been shown to be dominant in other common TCO systems.¹⁷ Here, we expand the picture by moving beyond the electrical property optimization point and investigate IO:H films with a wide range of N_e , μ , and percent hydrogen content (%H). By including films with a high hydrogen content, we identify and quantify contributions to μ from all likely scattering mechanisms, including grain boundary scattering, whose contributions have not previously been quantified in IO:H.

II. EXPERIMENTAL

Depositions of hydrogenated indium oxide (IO:H) were performed at École Polytechnique Fédérale de Lausanne (EPFL) following the procedure outlined in the work of Barraud *et al.*⁵ Sputtering of In₂O₃ targets of 99.9999% purity with an RF power density of ~ 5 W/cm² was performed in an argon atmosphere dosed with oxygen and water vapor, on AF32 Schott glass substrates. The total process pressure was maintained at 5 mTorr, with a base pressure of 1.5 μ Torr, and a constant $O_2/(O_2 + Ar)$ of 1% was maintained. A water vane was used to introduce a small flow of H₂O into the sputter chamber during depositions to incorporate H into the sputtered thin-films. This water vapor partial pressure, $p(H_2O)$, was varied from 0 to 8.5 μ Torr. Films deposited at each $p(H_2O)$ were split into two lots: one kept as-deposited for characterization and one subjected to an annealing process prior to characterization. For this second lot, annealing was performed at 200 °C for 20 min in an ambient atmosphere to simulate the processing that the TCO would undergo during the screen-printing step of silicon heterojunction solar cell fabrication.

Rutherford backscattering (RBS) spectrometry and Elastic Recoil Detection (ERD) using 2 MeV He ions were used to determine indium, oxygen, and hydrogen compositions in the films. Given the large uncertainty (10% of given values) of the measured hydrogen compositions, glow discharge optical emission spectroscopy (GDOES) was additionally used to determine In, O, and H amounts.

Scanning Electron Microscopy (SEM) imaging in an FEI Helios NanoLab 460F1 system was used to determine lateral grain sizes on the film surface and compared to bulk, vertical grain size estimations from X-ray Diffraction (XRD) patterns measured in the standard Bragg-Brentano configuration and probing throughout the entire thickness of the films. XRD was additionally used to quantify the amorphous fraction of the films before and after annealing. This phase quantification was possible by using the traditional Rietveld Refinement technique in the Materials Analysis Under Diffraction (MAUD) software.

Absorptance spectra were calculated from transmittance and reflectance data measured using a Perkin Elmer Lambda 950 UV vis-NIR spectrophotometer.

Room temperature Hall measurements of as-deposited and annealed IO:H films were completed in a Van der Pauw Ecopia HMS-3000 measurement system. Temperature-dependent Hall measurements of as-deposited and annealed IO:H films were taken using a Physical Property Measurement System (PPMS) Quantum Design, Inc. system using a typical Van der Pauw configuration with samples mounted in a J-Bend Evergreen Semiconductor chip carrier with the contact made using high purity silver paste. The system was cooled down to 5 K for the lowest temperature measurements using liquid helium.

III. RESULTS

A. Composition and structure

The results of RBS, ERD, and GDOES in Table I show a linear trend of the hydrogen content with $p(H_2O)$. RBS/ERD were only able to resolve the composition within 1%, leading to significant uncertainties in the %H content. We will therefore refer to the IO:H films by their GDOES-measured %H content. The IO:H film deposited with a $p(H_2O)$ of 0 shows a significant hydrogen amount was incorporated (2.7% H measured after annealing), indicating residual amounts of water vapor present in the sputter tool chamber despite evacuation down to levels of $\sim 3 \times 10^{-7}$ Torr

TABLE I. Values of indium, oxygen, and hydrogen compositions measured by Rutherford backscattering (RBS)/elastic recoil detection (ERD) and glow discharge optical emission spectroscopy (GDOES) after annealing at 200 °C and the fraction of amorphous content prior to the annealing of H-doped In₂O₃ films sputtered with varied $p(H_2O)$ measured by X-ray diffraction and quantified by the Rietveld Refinement technique. The film thickness of as-deposited films was measured using a profilometer and cross-sectional SEM.

$p(H_2O)$ (Pa)	RBS and ERD (at. %)			GDOES (at. %)			As-deposited Amorphous fraction (%)	Film thickness (nm)
	In	O	H	In	O	H		
0	43 $\pm$ 1	56 $\pm$ 2	<1 $\pm$ 1	42.6 $\pm$ 0.5	54.9 $\pm$ 0.7	2.7 $\pm$ 0.7	2 $\pm$ 2	254 $\pm$ 20
1.5	41 $\pm$ 1	54 $\pm$ 2	4 $\pm$ 1	40.3 $\pm$ 0.5	56.2 $\pm$ 0.7	3.9 $\pm$ 0.7	8 $\pm$ 3	238 $\pm$ 20
3.5	40 $\pm$ 1	54 $\pm$ 2	5 $\pm$ 1	43.7 $\pm$ 0.5	51.1 $\pm$ 0.7	5.2 $\pm$ 0.7	32 $\pm$ 17	223 $\pm$ 20
8.5	39 $\pm$ 1	53 $\pm$ 2	7 $\pm$ 1	39.5 $\pm$ 0.5	53.5 $\pm$ 0.7	7.0 $\pm$ 0.7	89 $\pm$ 13	197 $\pm$ 20

FIG. 1. Scanning electron microscopy images showing the surface morphology of In_2O_3 deposited with (a) 0 μTorr , (b) 1.5 μTorr , (c) 3.5 μTorr , and (d) 8.5 μTorr $p(\text{H}_2\text{O})$, resulting in the varied hydrogen content and grain size. Films shown here have been annealed at 200 °C.

prior to depositing. It has been shown previously that manipulation of pumping time is a viable method of controlling the H content in IO:H.¹⁸ $p(\text{H}_2\text{O})$ present in the chamber also affected the thickness of the resulting films. Films measured using a profilometer and cross-sectional SEM (not shown) were 220 ± 20 nm, with the thickness of the films slightly decreasing with increasing $p(\text{H}_2\text{O})$, as reported in Table I. This decreasing thickness is attributed to a decreased sputtering efficiency with increasing water partial pressure present in the chamber.

While grain sizes are typically influenced by the film thickness, e.g., larger grain sizes in thicker films due to preferential grain growth, the effect of the thickness is negligible here as the thickness variation as measured using a profilometer is slight. Grain size differences therefore stem from the varied H content. Surface imaging by SEM reveals a decrease in lateral grain size with the increasing hydrogen content, as shown in Fig. 1. Grain size estimates were obtained by approximating the grains as spherical. SEM imaging shows a relatively little change in lateral, surface grain size when comparing as-deposited films and post-annealing (as-deposited SEM images not shown). X-ray diffraction (XRD) similarly shows a relatively little change in vertical, bulk grain size during annealing. The bulk grain size was obtained from XRD using the Scherrer formula,^{19,20} which provides the vertical grain size. A comparison of lateral, surface grain size estimated by SEM to vertical, bulk grain size estimated by XRD is shown in Fig. 2. The dependence of grain size on water vapor during sputtering has been previously observed in the In_2O_3 system, where higher H_2O concentrations lead to regions where crystallization was suppressed.^{21–23} The indexed XRD spectra measured for as-deposited and annealed films

are shown in the [supplementary material](#). An increasing amorphous fraction of the as-deposited films is observed with the increasing %H content. Upon annealing, the higher %H content films show an increase in the number of XRD reflections. While H suppresses crystallization upon deposition, it appears to additionally increase the number of nucleation sites for grains such that upon annealing, a multitude of grains develop out of the amorphous portion of the films.

B. Optical performance

The transmittance and reflectance spectra of the IO:H-glass stack were measured using a spectrophotometer,

FIG. 2. Grain size estimates of IO:H films, from x-ray diffraction and scanning electron microscopy. 7.0% H IO:H films were measured to be largely amorphous in the as-deposited condition.

allowing the evaluation of the films' absorptance by the relationship

$$1 - (R + T) = A, \quad (2)$$

where R is the reflectance, T is the transmittance, and A is the absorptance. Features present in the UV-vis portion of the transmittance data are interference fringes caused by differences in the thickness of the films (thickness noted in Table I). A in the red-to-infrared region, i.e., FCA, appears to trend inversely with the hydrogen content as shown in Fig. 3. These changes in FCA come from the significantly different electrical properties of the films and specifically large changes of μ vs. %H rather than N_e vs. %H, as is discussed further in Sec. IV.

C. Electrical performance

The room-temperature N_e and μ are shown in Figs. 4(a) and 4(b), respectively. Inspection of N_e reveals several notable behaviors. For the as-deposited IO:H films, N_e initially increases with the increasing hydrogen content. This is expected, as previous authors have suggested that H acts as a donor in the In_2O_3 system.²⁴ Upon annealing, N_e decreases, and for films with intentionally introduced hydrogen, N_e is reduced by a factor of approximately 3.

μ is also greatly affected by both the hydrogen content and the annealing process. μ is maximized at ~5% H both for the as-deposited and the annealed films. Following the μ maximum, it decreases by an order of magnitude when %H increases to 7.0%. For films deposited with ~5% or less hydrogen, the room-temperature μ doubles upon annealing as shown in Fig. 4(b), whereas the films with the ~7% H content show no significant change after annealing. The doubling of μ of IO:H upon annealing has previously been observed and attributed to grain growth and crystallization during annealing,^{6,7} but this explanation is not wholly satisfactory, particularly since films in our sample set with ~3–4% H are nearly fully crystalline upon deposition, yet a doubling of μ is still achieved. The in-grain transport property changes upon annealing are therefore worth inspecting as the cause of the μ increase.

FIG. 3. Transmittance (solid lines) and absorbance (dashed lines) of IO:H thin-films post-annealing at 200 °C for 20 min.

FIG. 4. (a) Carrier density and (b) mobility of IO:H thin-films as-deposited and post-annealed at 200 °C for 20 min. Error bars are contained within the marker size, and error stems from measuring multiple, co-deposited samples.

Free carrier transport properties depend upon scattering mechanisms present in the film. Mechanisms typically implicated are ionized impurity scattering (IIS), phonon scattering, and grain boundary scattering.^{17,25} The theories developed around these show different temperature dependencies, and to disentangle the influence of these mechanisms in IO:H, measuring μ vs. temperature becomes necessary. Figure 5(a) shows μ measured from 5 to 300 K. The 2.7% H film is temperature independent over the full temperature range, while the 3.9% H and 5.2% H films show a decreasing μ at higher T. For the 3.9% H film, the range over which μ decreases is small: 250–300 K. The 5.2% H film shows a decreasing μ over a larger range: 80–300 K. The 7.0% H film shows an increase in μ with increasing temperatures in the range of 20–150 K, while from 150 to 300 K, μ remains fairly temperature-independent. It was not possible to obtain a measurement below 20 K for the 7.0% H film, as σ decreased below the measurement limit of the PPMS tool.

The temperature dependence of N_e was simultaneously obtained during the Hall measurement and is shown in Fig. 5(b). For nearly all films observed, N_e remains relatively constant over the entire temperature range, confirming that these TCOs are degenerate semiconductors. The exception is the annealed film with the highest hydrogen content, which shows that N_e strongly increases at temperatures below 140 K. This is very unusual behavior as non-degenerate semiconductors generally show an increasing N_e with increasing T , as E_F moves away from the conduction band minimum and toward the midgap. This behavior was

FIG. 5. Temperature-dependent (a) mobility and (b) carrier density for IO:H films. Error bars are contained within the marker size, and error stems from multiple measurements on the same sample with uncertainties arising from switching measurement polarity. Dashed lines in (b) are guides for the eye.

repeatedly measured. A possible explanation may be a high concentration of electron traps becoming active below 140 K.

IV. DISCUSSION

Both Figs. 4(a) and 5(a) indicate that all IO:H films are degenerate, meaning that all states up to the conduction band minimum are filled. This remains true despite a strong reduction of N_e upon annealing. The decrease in N_e post-annealing seen in Fig. 4(a) may stem from either the annihilation of oxygen vacancies—as the n-type conductivity in In_2O_3 has historically been attributed to the abundance of oxygen vacancies in the material^{26,27}—or the out-gassing of hydrogen, which has been suggested to be the dominant donor in the IO:H system.²⁴ Further studies to approximate the population of oxygen vacancies and track the hydrogen content during annealing are necessary to confirm the cause of the N_e decrease.

Comparison of the transmittance and absorptance shown in Fig. 3 with N_e shown in Fig. 4(a) reveals that free carrier absorption (FCA) in the red to infrared range of the spectrum does not trend with N_e . While the IO:H film displaying the lowest N_e shows the lowest measured absorptance, the IO:H film with the highest N_e also shows low absorptance and a

greater transmittance over a large portion of the measured spectrum. While N_e strongly influences the onset wavelength of FCA,^{28,29} termed the plasma frequency (ω_P),³⁰ the strength of absorption is additionally affected by μ —more specifically, the absorption strength is affected by the scattering mechanisms which dictate the scattering time (τ) and subsequently μ . The relationship between ω_P , τ , and μ is defined by the extended Drude model,³¹ defined in the [supplementary material](#), Eqs. (1a)–(4), which includes a damping constant $\Gamma(\omega)$ that is frequency-dependent. This is necessary when considering scattering from charged impurities, which introduces a frequency-dependence to the damping constant. Charged impurity scattering, common in highly doped semiconductors, is discussed in Sec. IV A.

We would expect ω_P to increase with increasing N_e [according to Eq. (2a) in the [supplementary material](#)], thus causing greater FCA at smaller wavelengths. However, this trend is not observed in Fig. 3 when considering N_e in Fig. 4(a).

We must instead consider the scattering time τ and specifically the effect of the scattering mechanisms on μ . Reduced FCA observed for the 5.2% H film with high N_e indicates that this film has a higher μ , potentially stemming from reduced carrier scattering present in the film.

A. Review of common mobility models for TCOs

To analyze the temperature-dependent mobility measurements shown in Fig. 5(a), we considered scattering mechanisms common to polycrystalline TCOs: ionized impurity scattering, phonon scattering, and grain boundary scattering. Neutral impurity scattering is an additional mechanism that can affect transport in semiconductors, but here we consider it insignificant compared to ionized impurity scattering due to the scattering cross-sections of the neutral impurities.³²

As all of our films appear degenerate, we use the Brooks-Herring-Dingle formulation to describe the ionized impurity scattering mobility (μ_{iis} , shown explicitly in the [supplementary material](#), Eqs. (5a) and (5b)).^{17,33,34} Since the Fermi level sits above the conduction band for degenerate semiconductors, N_e and the density of ionized impurities, N_i , are assumed not to vary with temperature, causing μ_{iis} to be temperature independent. This is supported by the approximately flat N_e observed in Fig. 5(b).

Phonon scattering can arise from acoustic or optical phonons. Polar optical phonon scattering [*POPS*, mobility equations shown explicitly in the [supplementary material](#), Eqs. (6a) and (6b)] has been shown to be the dominant contributor in undoped In_2O_3 ,³² and we follow the Howarth-Sondheimer³⁵ and Ehrenreich³⁶-based derivations detailed by Seeger^{37,38} for the polar optical phonon mobility (μ_{pops}), which shows a $e^{(\frac{1}{T})}$ temperature dependence, where T is the temperature in Kelvin.

For thermionic emission grain boundary scattering (*GBS*), the model derived by Bruneaux³⁹ from Fermi-Dirac statistics suitable for degenerate semiconductors was used to describe the grain boundary scattering mobility [μ_{gbs} , Bruneaux, relevant equations shown explicitly in the [supplementary material](#), Eqs. (8a) and (9b)]. The potential barrier height at a

grain boundary is well-described by Seto [shown explicitly in the [supplementary material](#), Eqs. (7c) and (7d)],^{40,41} and the difference between the Fermi level and conduction band minimum ($E_F - E_C$), necessary to evaluate the potential barrier height, was approximated according to the Joyce-Dixon model for degenerate semiconductors [equations shown explicitly in the [supplementary material](#), Eqs. (9a) and (9b)].⁴² Using these above formulations for scattering mechanisms, the total mobility of the IO:H films can be expressed as follows, as given by the Matthiessen rule:⁴³

$$\frac{1}{\mu_{total}} = \frac{1}{\mu_{iis}} + \frac{1}{\mu_{pops}} + \frac{1}{\mu_{gbs, Bruneaux}}. \quad (3)$$

B. Scattering mechanisms limiting mobility in IO:H

Excellent fits of the data in Fig. 5 using Eq. (3) show that the mobility of IO:H can be well described by ionized impurity scattering (*IIS*), polar optical phonon scattering (*POPS*), and grain boundary scattering (*GBS*); these fits are provided in the [supplementary material](#), with constants in Table I and fit parameters in Table III.

To clarify the individual impact of *IIS*, *POPS*, and *GBS*, the fractional contributions of each mechanism were calculated and are shown in Fig. 6. It is evident from Fig. 6 that *IIS* is dominant across the full temperature range for nearly all films. However, the influence on μ_{total} from *POPS* and *GBS* is quite large despite the small fractional contributions to $\frac{1}{\mu_{total}}$. For example, the *POPS* and *GBS* summed contribution to $\frac{1}{\mu_{total}}$ for the 5.2% H film reaches a combined

FIG. 6. Ratio of reciprocals of fitted ionized impurity scattering mobility, phonon scattering mobility, and grain boundary scattering mobility to the reciprocal of fitted total mobility. Symbols indicate the scattering mechanism inspected and indicate the temperature at which a Hall measurement was taken. Text indicates whether the films remain as-deposited or annealed at 200 °C.

maximum of $\sim 20\%$. However, this causes a significant mobility reduction from $\sim 120 \text{ cm}^2/\text{Vs}$ at temperatures below 100 K to $>100 \text{ cm}^2/\text{Vs}$ at room temperature. It is evident that sensitivity to *POPS* and *GBS* increases as μ_{iis} increases. A crossover point occurs between 5% and 7% H when the mobility becomes dominated by *GBS*. This is readily explained by the trend of the grain size dependence on the hydrogen content shown in Fig. 2—the exact crossover point from *IIS*-limited to *GBS*-limited lies near 10 nm. This is supported by calculating the mean free path of the electron,²⁵ shown in Table IV in the [supplementary material](#), which shows that the grain size begins to rapidly approach the mean free path length at a higher hydrogen content.

The IO:H films deposited with $\sim 5\%$ H and $\sim 7\%$ H show very different mobility behaviors with temperature before and after the annealing process. The contributions from *POPS* remain fairly consistent in the 5% H film, but *GBS* contributions become far more prominent upon annealing in both 5% and 7% H cases. This suggests that grain boundaries are created during crystallization, despite only slight grain size differences observed by SEM and XRD before and after annealing.

When considering the components contributing to the mobility of IO:H, it is clear that the increase in μ_{total} to the maximum mobility point is caused by an increase in the μ_{iis} component. The reason is not immediately clear however. Considering the Brooks-Herring-Dingle³⁴ formulation [given in the [supplementary material](#), Eq. (5a)], μ_{iis} shows a dependence upon the square of the charge state of the impurity (Z), the ratio of N_e to N_i , the effective mass (m^*), and the screening function $F_{ii}(\xi_\delta)$. As the non-parabolicity of the conduction band is accounted for,³³ $F_{ii}(\xi_\delta)$ can be simplified as $\propto \ln(N_e^{\frac{1}{3}})$. Increasing N_e increases $F_{ii}(\xi_\delta)$ but causes μ_{iis} to decrease and therefore cannot be the cause of the μ_{iis} increase. Regarding m^* , previous studies have found $\frac{m^*}{m_0}$ to be 0.33 ± 0.05 ,⁴⁴ while others found a value of 0.22 ± 0.02 .^{7,32} However, the increase in μ_{iis} with increasing %H cannot be accounted for by changes in $\frac{m^*}{m_0}$ from 0.33 to 0.22.

This leaves two possibilities: either Z must decrease or N_i must decrease. A decreasing N_i with an increasing N_e is unlikely, particularly as previous authors²⁴ suggest that hydrogen is a donor in the system. It is instead quite possible that as H% increases across our sample set, we transition from a regime where oxygen vacancies are the dominant donor to a regime where hydrogen is the dominant donor, meaning that Z transitions from +2 to +1. To visualize this, we calculated and plotted N_e vs. μ_{iis} for both $Z = +1$ and $+2$ [using the Brooks-Herring-Dingle formulation, given in the [supplementary material](#), Eq. (5a)] and compared to the values shown in Fig. 4, which are re-plotted in Fig. 7. Clearly, the as-deposited and annealed films with $\sim 3\%$ – 4% H fall in a regime where Z is likely +2, leading to a lower μ_{iis} , whereas the annealed $\sim 5\%$ H film falls exactly on the $Z = +1$ line. Interestingly, this film prior to annealing falls slightly below this line, indicating that perhaps during annealing, oxygen vacancies are annihilated and hydrogen is activated to become the dominant donor. The $\sim 7\%$ H films

FIG. 7. Calculation and measurement of the room-temperature carrier density and mobility of IO:H films with the varied hydrogen content, both as-deposited and annealed. Calculated mobility lines are purely from ionized impurity scattering with the solid line having a fixed impurity charge state of $Z = +1$ and the dotted line with $Z = +2$.

deviate strongly from either calculated line as grain boundary scattering strongly influences these films in addition to ionized impurity scattering.

Sensitivity to GBS and $POPS$ increases when μ_{iis} is increased. GBS can be readily reduced by ensuring large grain sizes during growth and annealing,⁴⁵ but considering the Seeger formulation,^{37,38} $POPS$ reduction may not be so easily achieved. μ_{pops} depends upon the Seeger constant [S , defined explicitly in the [supplementary material](#), Eq. (6b)], the Debye temperature (θ_D), and the temperature (T). The reported values of θ_D range from 420 K (Ref. 46) to 811 K,^{32,47} and varying between these values has a considerable impact on $POPS$ and therefore μ_{pops} above 150 K. Our fits result in θ_D values of 430–1131 K, with the largest value corresponding to the film with the highest mobility. However, the complexity of the phonon spectrum due to the large, 80-atom unit cell of In_2O_3 ⁴⁸ results in many longitudinal optical phonon modes of varied phonon energy,⁴⁷ meaning that θ_D cannot be assigned a single phonon energy, and the θ_D values are instead an effective θ_D which describes μ_{pops} . This is a difficult parameter to control in such a complex structure and does not provide a path to reducing $POPS$.

To further inspect the S constant influencing μ_{pops} , a similar evaluation to that done with μ_{iis} is applied. Rather than fixing S values to those from the fits, S is instead calculated over broad ranges of $0.01 < K < 1$ and $0.22 < \frac{m^*}{m_0} < 0.33$. The effective dielectric constant (ϵ^*) is calculated as $\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_r}$, with values for ϵ_∞ and ϵ_r ranging from 3.8 to 4^{31,44} and 8.9 to 9,^{49,50} respectively. The 5% H, as-deposited film has a significant contribution of $POPS$, yielding $S = 1336 \pm 83$. This corresponds to K values in the range of 0.05–0.1. (For most polar semiconductors,³⁷ K^2 is on the order of 10^{-3} ; for high-quality piezoelectric materials, the values have been reported as high as 0.9.⁵¹) K is a dimensionless ratio which represents a measure of the conversion efficiency between mechanical and electrical energies, and the values approaching 1 are possible for materials with low stiffness. As $\mu_{pops} \propto S \propto K^{-3/2}$, the values of K approaching 1 are preferable to maximize S and ultimately μ_{pops} . The low K values

FIG. 8. Interpolating between fitted Hall mobility data for the hydrogen content vs. temperature (K) for IO:H films. Measured data points are indicated by a white $\circ$. The region where $1/\mu_{gbs} : 1/\mu_{total} \geq 5\%$ is indicated by a diagonal down right pattern. The region where $1/\mu_{pops} : 1/\mu_{total} \geq 5\%$ is indicated by a diagonal down left pattern. In the overlapping region, indicated by crosshatch pattern, $1/\mu_{gbs}$ and $1/\mu_{pops}$ contribute $\geq 10\%$ to $1/\mu_{total}$. In all other regions, $1/\mu_{iis} : 1/\mu_{total} > 95\%$.

estimated here in In_2O_3 perhaps highlight an area to explore increasing μ_{total} at device operating temperatures, where μ_{pops} plays a significant role.

The model using μ_{iis} , μ_{pops} , and μ_{gbs} having aptly described our measured mobility data, total mobility values across our temperature measurement range were interpolated across a range of 1.5%–7% H using the fit parameters from the annealed IO:H films, resulting in Fig. 8.

The regions highlighted indicate $\geq 5\%$ individual contributions of either the reciprocal of μ_{pops} or μ_{gbs} to the reciprocal of μ_{total} . The remaining areas outside the indicated $POPS$ and GBS regions have $>95\%$ contributions from μ_{iis} . In Fig. 8, it is seen that $POPS$ begins to play a role at temperatures above 150 K in the range of IO:H films containing ~ 2 –5.2% H. With effective ϕ_D estimated as 420–1131 K (corresponding to phonon energies of 36–97 meV), the phonon population at temperatures below 150 K (<13 meV) is negligible in regard to impacting carrier transport.

In contrast, the temperature range of significant GBS becomes far more broad as H% is increased. This is due to the decreased grain size at a higher H content, where μ_{total} becomes restricted by low μ_{gbs} .

It is interesting to note the highest μ_{total} obtained at room temperature occurs in the overlap between $POPS$ and GBS regions. This again demonstrates how sensitivity to GBS and $POPS$ is increased as IIS is decreased. The region of the highest μ_{total} occurs outside the influence of GBS and $POPS$, indicating that higher μ_{total} values at room temperature are possible if μ_{gbs} and μ_{pops} can be increased at these temperatures.

V. CONCLUSION

By investigating the temperature-dependent mobility behavior of IO:H over a wide range of hydrogen incorporation, we found that ionized impurity scattering dominates electron transport. However, sensitivity to polar optical phonon scattering is greatly increased as scattering from ionized impurities is reduced, particularly above 150 K. Grain boundary scattering becomes dominant when grain sizes

approach 10 nm—meaning that the free path length of the electrons approaches the grain size—which was observed at 7% H incorporation. It was also seen that grain size is reduced with the increasing hydrogen content in the film. Quantification of the influence from ionized impurity scattering, phonon scattering, and grain boundary scattering was accomplished by use of the Matthiessen rule,⁴³ where the reciprocals of the mobilities sum to the reciprocal of total mobility. Even in regions where the reciprocal of phonon or grain boundary scattering was a small fractional contribution (5%–20%) to the reciprocal of total mobility, these scattering mechanisms still significantly impact the total mobility of the films.

The observed reduction of ionized impurity scattering with increasing hydrogen is attributed to a decrease in the charge state from +2 to +1 as the dominant donor in the system transitions from oxygen vacancies to hydrogen donors. This allows a maximization of the μ_{iis} component, enabling high mobilities observed at ~5% H contents. Mobility does not seem to be affected by inactive hydrogen in the film as neutral impurity scattering was not found to be significant.

Modeling of polar optical phonon scattering revealed effective Debye temperatures in the range $\phi_D = 420$ –1131 K and electromechanical coupling constant $K = 0.05$ –0.1. These estimated low K values limit the upper threshold of μ_{pop} and stem from the polar nature of the In_2O_3 structure. Higher K values of up to 0.4 have been reported in TCOs such as ZnO ,⁵² which has strong piezoelectric characteristics due to its typically wurtzite structure, indicating that this could be a system where higher mobilities than IO:H may be attained once ionized impurity and grain boundary scattering are suppressed.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for indexed X-ray diffraction spectra of as-deposited and annealed thin films of hydrogenated indium oxide with varied hydrogen contents, measured and modeled Hall mobility data for 2.7% H, 3.9% H, 5.2% H, and 7.0% H annealed and 5% and 7% as-deposited IO:H films, extended Drude model equations for the real and imaginary portions of the dielectric constant, equations defining μ_{iis} , μ_{pops} , and μ_{gbs} for both degenerate and non-degenerate semiconductors, tables providing both constants and fit parameters for mobility fits, and a table comparing IO:H grain size with the calculated electron mean free path.

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