Experimental and theoretical evidence for hydrogen doping in polymer solution-processed indium gallium oxide

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The field-effect electron mobility of aqueous solution-processed indium gallium oxide (IGO) thin-film transistors (TFTs) is significantly enhanced by polyvinyl alcohol (PVA) addition to the precursor solution, a >70-fold increase to 7.9 cm2/Vs. To understand the origin of this remarkable phenomenon, microstructure, electronic structure, and charge transport of IGO:PVA film are investigated by a battery of experimental and theoretical techniques, including In K-edge and Ga K-edge extended X-ray absorption fine structure (EXAFS); resonant soft X-ray scattering (R-SoXS); ultraviolet photoelectron spectroscopy (UPS); Fourier transform-infrared (FT-IR) spectroscopy; time-of-flight secondary-ion mass spectrometry (ToF-SIMS); composition-/processing-dependent TFT properties; high-resolution solid-state 1H, 71Ga, and 115In NMR spectroscopy; and discrete Fourier transform (DFT) analysis with ab initio molecular dynamics (MD) liquid-quench simulations. The Ga4+(H) rotational-echo double-resonance (REDORE) NMR and other data indicate that PVA achieves optimal H doping with a Ga–H distance of ~3.4 Å and conversion from six- to four-coordinate Ga, which together suppress deep trap defect localization. This reduces metal-oxide polyhedral distortion, thereby increasing the electron mobility. Hydroxyl polymer doping thus offers a pathway for efficient H doping in green solvent-processed metal oxide films and the promise of high-performance, ultra-stable metal oxide semiconductor electronics with simple binary compositions.

Significance

Solution processing of high-performance, high-Ga-content IGO thin-film transistors (TFTs)—or compositionally simpler and, hence, technologically more desirable indium gallium oxide (IGO) TFTs—remains challenging and an impediment to manufacturing low-temperature solution-processed MO electronics.

A morphous metal oxide (MO) semiconductors are of great fundamental scientific and technological interest due to their large band gaps and high electron mobilities (1–4), making them promising candidates for next-generation transparent and flexible electronics (5–9). Among these materials, indium gallium zinc oxide (IGZO) is by far the most investigated and technologically relevant, providing mobilities of 10 to 100 cm2/Vs

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The authors declare no competing interest.

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This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2007897117/-/DCSupplemental.

Here, we report an approach to enhancing electron mobilities in amorphous IGO (a-IGO) to levels approaching those in sputtered IGZO TFTs. Specifically, adding a hydroxyl-rich polymer, polyvinyl alcohol (PVA), to IGO (In:Ga = 6:4 mol ratio) precursor solutions yields IGO TFTs with mobilities as high as 7.9 cm²/Vs for films processed at 300 °C. The microstructure, electronic structure, doping effects, and charge transport of IGO:PVA films are characterized by a battery of techniques, including In K-edge and Ga K-edge extended X-ray absorption fine structure (EXAFS); high-resolution solid-state (SS) ¹H, ⁷¹Ga, and ¹¹⁵In NMR spectroscopy; resonant soft X-ray scattering (R-SOXS); ultraviolet photoelectron spectroscopy (UPS); Fourier transform-infrared (FT-IR) spectroscopy; time-of-flight secondary-ion mass spectrometry (ToF-SIMS); and composition-processing-dependent TFT properties, in concert with discrete Fourier transform (DFT) analysis and ab initio molecular dynamics (MD) liquid-quench simulations. Together, these provide evidence for H doping and -OH bonding effects that enhance mobility and electron-trap decoherence and represent a strategy for doping solution-processed MO semiconductors as well as fundamental insights of the doping mechanism.

**Results**

**IGO:PVA Film Growth and Characterization.** Solutions of MO film precursors In(NO₃)₃ and Ga(NO₃)₃ in deionized (DI) water, having x wt. % (used hereafter to denote mass %) PVA vs. IGO (x = 0 to 14), were spin-coated onto cleaned substrates and annealed at 300 °C for 30 min. This process was repeated three times to achieve film thicknesses of ~10 nm. PVA was chosen due to its solubility in the aqueous precursor solutions, high OH group content, and low acidity. All films are ultrasmooth with r.m.s. roughness (σRMS) ≤ 0.19 nm by atomic force microscopy (AFM) (Fig. L4), are completely amorphous by grazing incidence X-ray diffraction (GIXRD) (Fig. 1B), and exhibit relatively large M–O–M lattice content (>70% for <12 wt. % PVA) by X-ray photoelectron spectroscopy (XPS) (Fig. 1C). Moreover, the carbon content of the IGO:PVA films measured by using XPS never exceeds 4.0 at. % (Fig. 1D). See SI Appendix, Figs. S1–S9 and Tables S1–S3 for AFM, GIXRD, and XPS data. These results indicate that much of the PVA is thermolysed during annealing, and all IGO:PVA films have relatively large M–O–M lattice content, offering the potential to form high-performance MO TFTs with a high degree of uniformity over large areas.

**IGO:PVA TFT Characteristics.** To probe the electronic effects of PVA addition on IGO films, bottom-gate, top-contact IGO:PVA TFTs were characterized (see Materials and Methods for fabrication details). As shown in Fig. 2A, the IGO:PVA TFT transfer curves strongly depend on the PVA content, with tremendous on-current (I_ON; drain current measured at V_DS = V_GS = +80 V) and turn-on voltage (V_ON) variations. I_ON and V_ON data extracted from the forward-transfer curves are summarized in Fig. 2B. Neat IGO TFTs have low I_ON values (6.62 ± 2.23 × 10⁻⁷ A) and large positive V_ON values (+33.7 ± 12.3 V). With increasing PVA content from 0 to 8 wt. %, I_ON gradually rises (V_ON falls) to 1.25 ± 0.10 × 10⁻⁷ A (to ~6.2 ± 2.1 V) for an 8 wt. % PVA loading, exhibiting >1000x I_ON enhancement. Further addition of PVA to 14 wt. % depresses I_ON (increased F_COND) to 4.81 ± 0.31 × 10⁻⁸ A (to +38.1 ± 5.2 V). For all devices, I_DSS remains in the range of ~10⁻¹⁰ A, indicating relatively low carrier concentrations, suitable for low-power-consumption TFTs. Furthermore, PVA addition strongly suppresses hysteresis (ΔV_TH < 2 V with 8 wt. % PVA) vs. that in neat IGO TFTs, where ΔV_TH ~ 30 V, indicating that optimal PVA addition substantially suppressed the trap density of IGO films and, hence, enhanced TFT performance.

The mobilities in saturation and V_TH of IGO films were next extracted from the transfer plots (27), and data are shown in Fig. 2C and SI Appendix, Table S4. While neat IGO TFTs have an electron mobility of 0.10 ± 0.04 cm²/Vs, that in IGO:PVA TFTs maximized at 6.43 ± 0.73 cm²/Vs for 8 wt. % PVA. To our knowledge, this is one of the highest reported values for high-Ga-content, solution-processed IGO films annealed at 300 °C or lower (see SI Appendix, Table S5 for comparisons to literature data). For larger PVA content, the mobility falls (1.25 ± 0.66 cm²/Vs for 14 wt. % PVA), but remains higher than that in neat IGO. Similar to V_ON, V_TH first falls from +36.4 ± 9.2 V (0 wt. % PVA) to +16.6 ± 2.7 V (8 wt. % PVA) and then rises to +50.4 ± 5.5 V (14 wt. % PVA). Low V_TH in TFT is essential for low-power-consumption and low-driving-voltage applications (28). A lower processing temperature of 250 °C for IGO:PVA films was also investigated, and the performance enhancement of the corresponding TFTs is identical (SI Appendix, Fig. S10 and Table S6). Thus, optimization of the process as well as exploring other polymers may reduce the processing temperature even further. These TFT data indicate that PVA incorporation efficiently reduces electron charge-trap density in IGO and enhances mobility. This conclusion is supported by UPS and optical spectroscopic data (SI Appendix, Figs. S11–S13 and Table S7), which reveal that embedding PVA in IGO matrices lowered the work function (i.e., up-shifted the Fermi level).

**IGO:PVA Film Microstructure.** X-ray reflectometry (XRR) measurements were first carried out to analyze the microstructure of MO films as a function of PVA content. The average electron density and film thickness fall gradually from 1.42 e/Å³ and 10.2 nm (0 wt. % PVA) to 1.30 e/Å³ and 8.8 nm (14 wt. % PVA) (Fig. 3A and SI Appendix, Fig. S14 and Table S8). Next, EXAFS studies focused on atomistic microstructure details of IGO:PVA films and reveal few obvious absorption-profile variations with increasing PVA content in either the In K-edge and Ga K-edge data (Fig. 3B). Both coordination numbers (N) and bond lengths (R) of the first shell, along with the Debye–Waller factors, which measure structural disorder or variation, were computed and are summarized in SI Appendix, Fig. S15 and Table S9. The In–O and Ga–O coordination numbers remain in a narrow, under-coordinated range of 4.91 to 5.22 and 3.55 to 3.69, respectively, without obvious variations with PVA content. Similar evolutions of the Debye–Waller factors were also observed for the In–Ga coordination number (see SI Appendix, Fig. S16 and Table S10).
are also found for the bond lengths, where the In–O first shell is 2.13 to 2.15 Å and that of the Ga–O first shell is 1.85 to 1.86 Å. While crystalline β-Ga2O3 has two close Ga–O distances of 1.85 Å (tetrahedral Ga) and 2.01 Å (octahedral Ga), only a single contact at ~1.85 Å is observed in IGO:PVa (15). Moreover, the first-shell Ga–O coordination number is ~3.6, indicating that most Ga ions occupy tetrahedral sites.

Next, RSoXS was utilized to determine whether and to what extent phase separation accompanies PVA incorporation. As shown in Fig. 3C, in both neat IGO film and in IGO:PVa films with 8 wt. % PVA, no obvious change in profile shape is observed at off-resonant as well as near-resonant energies, while a peak at 30 to 40 nm is present in both films, suggesting little or no differences in in-plane morphology. The results further support the evidence that PVA significantly thermolyzes during the film fabrication and does not introduce phase separation in the resulting oxide films, which is beneficial for electron transport.

Since the above analyses do not provide conclusive information on how PVA enhances IGO:PVa transport properties, the question arises as to whether the smallest element, H, is involved. Several studies have investigated H incorporation in MO semiconductors such as ZnO and IGZO and suggested that H may act as a shallower donor by forming M–H bonds or M2H3... (37). Therefore, H2 annealing (38) and H plasma treatment (31, 38, 39), to cite H-dope MO semiconductors (34), have been used to study the effect of PVA on enhancing IGO:PVa transport properties, the origin of the H in the IGO:PVa films. By monitoring the D concentration and D/H ratio in the ToF-SIMS depth profiling, no evidence of D incorporation is found in either the undoped films or films with 4 wt. %, 8 wt. %, and 12 wt. % PVA (42), even though NMR indicated rapid D/H exchange with PVA in solution (SI Appendix, Fig. S16). FT-IR spectra also reveal the absence of significant O–D stretching modes at ~2,600 cm$^{-1}$. Together, these results argue that the majority of H in the IGO films originates neither from the precursor solvent nor from the PVA, but, rather, from the ambient atmosphere during thermal precursor conversion to ~3-nm MO films and subsequent cooling in ambient with relative humidity = 30 to 50%. Additionally, the relative quantities of H vs. GaO$_2$ vs. OH (GaO$_2$ meaning the GaO$_2$– ion peak) for H$_2$O-processed films were assessed by ToF-SIMS depth profiling (Fig. 3D and SI Appendix, Fig. S17). Note that the Si wafer–IGO:PVa film interface is clearly observed, indicating a relatively uniform etching process. Comparison of the H vs. GaO$_2$ and OH vs. GaO$_2$ molar ratios in Fig. 3D indicate that pristine IGO films (no PVA) have the highest H and OH concentrations (H/GaO$_2$ ~ 0.5; OH/GaO$_2$ ~ 6) compared to the IGO:PVa films. Note also that the H and OH content are lowest for 4 wt. % and 8 wt. % IGO:PVa (H/GaO$_2$ ~ 0.2; OH/GaO$_2$ ~ 2), with both ratios increasing slightly for 12 wt. % PVA (H/GaO$_2$ ~ 0.3; OH/GaO$_2$ ~ 3).

The OH content in IGO:PVa films was further quantified by attenuated total reflection (ATR) FT-IR spectroscopy. As shown in Fig. 3E, on the bare SiO$_2$ substrates, O–H stretching modes are not evident, but only a very weak C–H stretching (~2,900 cm$^{-1}$), presumably from surface contamination. However, neat IGO films exhibit relatively strong O–H stretching mode(s) at 3,200 to 3,600 cm$^{-1}$, centered near ~3,470 cm$^{-1}$.

To quantify the nature and amount of H in the present IGO:PVa films, ToF-SIMS depth profiling and FT-IR spectroscopy were first applied to the IGO:PVa precursors and IGO:PVa films annealed at 300 °C, with careful experimental design. For ToF-SIMS depth-profile measurements, IGO:PVa films were grown identically to those for TFT fabrication, but using D$_2$O rather than H$_2$O as the solvent to understand the origin of the H in the IGO:PVa films. By monitoring the D concentration and D/H ratio in the ToF-SIMS depth profiling, no evidence of D incorporation is found in the undoped films or films with 4 wt. %, 8 wt. %, and 12 wt. % PVA (42), even though NMR indicated rapid D/H exchange with PVA in solution (SI Appendix, Fig. S16). FT-IR spectra also reveal the absence of significant O–D stretching modes at ~2,600 cm$^{-1}$. Together, these results argue that the majority of H in the IGO films originates neither from the precursor solvent nor from the PVA, but, rather, from the ambient atmosphere during thermal precursor conversion to ~3-nm MO films and subsequent cooling in ambient with relative humidity = 30 to 50%. Additionally, the relative quantities of H vs. GaO$_2$ vs. OH (GaO$_2$ meaning the GaO$_2$– ion peak) for H$_2$O-processed films were assessed by ToF-SIMS depth profiling (Fig. 3D and SI Appendix, Fig. S17).

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increased H-bonding is detected on PVA incorporation. Regarding Ga0 wt. %, 4 wt. %, 8 wt. %, and 12 wt. % PVA (see spinning (MAS) NMR spectra of four IGO:PVA powders with most intense 1H resonance centered at Table S10 and Fig. S18 for details) are shown in Fig. 4 incorporation range. Moreover, greater O−H stretching modes were detected near 3,450 cm−1, excluding the possibility that the OH features are due to free or physisorbed H2O (43). Regarding Ga−H stretching modes expected near 2,000 cm−1 (44), careful analysis of the FT-IR data reveals no features in this range, indicating that the dominant form of H here must be O−H. The weakened O−H stretching intensity in the IGO:PVA films with 4 wt. % and 8 wt. % PVA indicates a lower oxide group acidity in the M−O−H units, indicating greater O−H covalency, in accord with the FT-IR spectra (Fig. 3E), implying weaker O−H bonding in the IGO:PVA films with increasing PVA content. Surface OH− groups (δ ~1 ppm) (47) were also detected in all four samples. 

Next, one-dimensional 71Ga MAS NMR spectra of 0 wt. %, 4 wt. %, 8 wt. %, and 12 wt. % IGO:PVA powders were acquired and are shown in Fig. 4B and SI Appendix, Fig. S19 and Table S11. In accord with the EXAFS data (Fig. 3B), 71Ga MAS NMR reveals that the majority (>85%) of Ga sites are four-coordinate (GaIV) (48). As the PVA content increased, the six-coordinate Ga (GaVI) fraction gradually falls from 13.8% (pristine IGO) to 5.2% (4 wt. % PVA) to 1.3% (8 wt. % PVA), and to 0% (12 wt. % PVA) (SI Appendix, Table S11). The extremely large nuclear quadrupolar coupling constant, CQ, in all of the four samples indicates that Ga, especially GaIV, is in a severely distorted low-symmetry local environment. Fig. 4C shows rotational-echo double-resonance (REDOR) experiments on IGO:PVA powders. REDOR NMR acquired the reference signal SS (without dephasing pulses) and the dephased signal SD (with dephasing pulses ~180°) pulses on 1H) under rotor synchronization. The signal difference, ∆S = SD − SS, suggests the extent to which the observed 71Ga coherence was dephased due to 71Ga−1H spin−dipolar coupling interactions. The heteronuclear dipolar coupling constant extracted from REDOR measurements, dij, is strongly distance-dependent: dij ∝ 1/rij3, where rij is the distance between spins i and j. Therefore, the shorter the 71Ga−1H spin distance, the stronger the dipolar coupling, and thus, the greater the magnetization magnitude dephasing in the observed 71Ga coherence, i.e., the attenuated 71Ga (1H) REDOR signals. Information on 71Ga−1H spatial proximity can therefore be

Moreover, PVA addition to 4 wt. % and 8 wt. % IGO:PVA weakens the O−H mode again and shifts the peak to ~3,390 cm−1. Note that the C−H stretch at ~2,900 cm−1 remains unchanged in all samples and that no H−O−H bending modes were detected near 1,635 cm−1, excluding the possibility that the OH features are due to free or physisorbed H2O (43). Regarding Ga−H stretching modes expected near 2,000 cm−1 (44), careful analysis of the FT-IR data reveals no features in this range, indicating that the dominant form of H here must be O−H. The weakened O−H stretching intensity in the IGO:PVA films with 4 wt. % and 8 wt. % PVA indicates a lower oxide group acidity in the M−O−H units, indicating greater O−H covalency, in accord with the FT-IR spectra (Fig. 3E), implying weaker O−H bonding in the IGO:PVA films with increasing PVA content. Surface OH− groups (δ ~1 ppm) (47) were also detected in all four samples. 

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obtained from the normalized $\Delta S/S_0$ as a function of dipolar coupling time. As shown in Fig. 4D, the build-up rate of the $^{71}$Ga signal, $\Delta S/S_0$, decreased with higher PVA content. Considering the OH group O–H affinity suggested by the δ 5.4- to 4.6-ppm chemical shifts and the change in the broad $^1$H peak intensity, the more rapid build-up of $\Delta S/S_0$ in the 0 wt. % PVA-based IGO:PVA powder is expected. As the PVA content increases, the −OH in IGO:PVA powders lead to slower $^{71}$Ga dephasing by $^1$H. As shown in Fig. 4D, $\Delta S/S_0$ decreases from 0.56 (0 wt. % PVA), to 0.49 (4 wt. % PVA), to 0.44 (8 wt. % PVA), and to 0.38 (12 wt. % PVA) at a 0.5-ms dipolar decoupling time ($^1$T$_D$). The slower $\Delta S/S_0$ build-up in the IGO:PVA powders indicates ineffective dephasing of $^{71}$Ga magnetization. As seen in the $^1$H MAS (Fig. 4A) and IR (Fig. 3E) spectra, the O–H bonding in the IGO:PVA powders interferes with the dephasing process, while retaining higher S. Second-moment ($^1$M$_2$) REDOR data analysis within the $\Delta S/S_0 < 0.3$ range yields average Ga–H distances ($^1$A Appendix, Fig. S20), which increase from 3.23 ± 0.33 Å (0 wt. % PVA), to 3.30 ± 0.33 Å (4 wt. % PVA), to 3.36 ± 0.34 Å (8 wt. % PVA), and to 3.70 ± 0.37 Å (12 wt. % PVA). Note that the REDOR build-up curve suggests a distribution of Ga–H distances.

Next, $^{115}$In MAS NMR spectra of 0 wt. %, 4 wt. %, 8 wt. %, and 12 wt. % IGO:PVA powders were acquired and are shown in SI Appendix, Fig. S21. The $^{115}$In is a quadrupolar nucleus with spin 9/2 and has a large quadrupole moment ($^1$Q) of 77.0 fm$^2$ (49). Owing to large $^1$Q, the quadrupole interactions dominate, resulting in a very broad linewidth of >1 MHz, which introduces challenges in acquiring the full spectral range (50). The $^{115}$In NMR spectra are therefore displayed by overlaying each individual spectrum collected at evenly spaced resonant-frequency intervals of ±144 kHz. The resulting broad $^{115}$In resonances in all samples indicate similar In chemical environments in all of the IGO:PVA powders, in accord with the EXAFS results. By careful analysis of the spectra, the line-shape of $^{115}$In signal in the central transition is seen to slightly narrow upon PVA addition, implicating a falling In quadrupole coupling constant ($^1$C$_Q$) and, hence, a somewhat more uniform In environment. However, the line-shape deviates from a typical quadrupolar pattern (51) due to disorders in environments, which introduces challenges in spectral simulation to determine the exact magnitude of $^1$C$_Q$ (51).

Theoretical Analysis of IGO H Doping. Based on the above experimental results, theoretical analyses were performed to further elucidate H-doping effects in amorphous oxides and in IGO in particular. Amorphous In$_{32}$Ga$_{22}$O$_{79}$H$_1$ and In$_{32}$Ga$_{22}$O$_{80}$H$_1$ were prepared via ab initio MD liquid-quenches simulations and then doped with a single interstitialal H radical (see SI Appendix for details of this approach). First, it was found that the most energetically favorable configurations in both In$_{32}$Ga$_{22}$O$_{80}$H$_1$ and In$_{32}$Ga$_{22}$O$_{79}$H$_1$ corresponded to M–OH unit formation with $\sim$1.0 Å O–H bond lengths (Fig. 5A). This represents a strong covalent OH$^-$ bond, confirmed by a Bader-charge transfer analysis (Fig. 5A) and by the reduced O coordination number associated with weaker M–OH bonds (SI Appendix). Among the 40 cases with various H locations in IGO considered here, the higher-energy (less-favorable) configurations correspond to formation of interstitialal H, where the H radical gains an additional electron from neighboring metals to become H$^+$, indicated by the calculated charge transfer (Fig. 5B). The calculated formation energy (SI Appendix) suggests that at 300 K, concentration of H interstitials is $\sim$7 orders of magnitude lower than that of OH$^-$ in IGO$_{2.96}$.

To probe H-defect thermal stability and possible H mobility in a-IGO at 300 K, MD simulations were performed at 300 K for In$_{32}$Ga$_{22}$O$_{80}$H$_1$ and In$_{32}$Ga$_{22}$O$_{79}$H$_1$ (SI Appendix, Figs. S22–S25) by using the most energetically stable DFT configuration as the initial structure in each case (e.g., Fig. 5A). The MD simulations were run for $\sim$250 ps (i.e., 124,000 ab initio MD steps) for each structure, after which the position of H and the time spent bonded to a specific O or as an interstitial in the vicinity of a metal atom were determined and are plotted in Fig. 5C (In$_{32}$Ga$_{22}$O$_{80}$H$_1$) and Fig. 5D (In$_{32}$Ga$_{22}$O$_{79}$H$_1$). Clearly, the H behavior at 300 K differs significantly in the two structures, having different O stoichiometries and different amounts of four-coordinate Ga (see SI Appendix, Figs. S22–S25 for details). The facile diffusion of H in In$_{32}$Ga$_{22}$O$_{80}$H$_1$ is the result of large fluctuations in the neighboring M–O bonds that make the potential wells rather shallow and increase the H probability to travel through the disordered structure. While in In$_{32}$Ga$_{22}$O$_{79}$H$_1$, H spent more than 11 times longer (115 ps) bonded to the O atom with the lowest effective coordination number when 300 K MD simulations were initiated using the most stable 0 K DFT position in In$_{32}$Ga$_{22}$O$_{79}$H$_1$.
The reason for the more uniform conduction charge density is a better hybridization due to weakening of the strongest Ga–O bonds and the resulting decreased distortions in all MO polyhedrals with attached OH⁻. The observed vigorous H diffusion at room temperature (Fig. 5C) is expected to facilitate the carrier-transport enhancement in the material since H spends enough time bonded to each O to optimize the local structure in its vicinity.

Furthermore, the presence of H reduces the localization of deep electron traps (SI Appendix, Fig. S27). In Fig. 5E, the calculated charge-density distributions for the deep trap defects in H-free and H-doped In₃₂Ga₂₂O₇₉ are shown. Before H doping, the trapped electron was localized between two undercoordinated, undershared In atoms, located at 2.82 Å from each other. Upon OH⁻ formation, the trapped charge density was found at two separate locations, the initial In–In pair (now at 2.78 Å) and a new one, with the In–In distance of 2.72 Å, which is significantly shorter compared to the 3.30 Å for these atoms in the H-free structure. The reason for the second short-distant In–In pair to form is a reduction of the In coordination from 4 to 3, suggesting an equal probability to find the electron in either of the two locations. Indeed, the localization of the deep defect decreases by almost one-half, as compared to the H-free case (SI Appendix, Fig. S27). This finding along with more uniform charge density within the conduction band agrees with the results from the optical and UPS data (SI Appendix, Table S7), where an $E_F$ upshift was observed with PVA incorporation, and explains the greater electron mobility in IGO:PVA.
Role of Ga and PVA in H Doping. To further understand the combined role of Ga and PVA in the H-doping process and the resulting TFT charge transport, a series of additional MO matrices having different metal compositions or different organic additives (polyvinyl phenol [PVP] and glycerol [Gly]) were investigated to replace PVA (Fig. 6 and SI Appendix, Figs. S28–S39). Previously, we reported that PVA suppresses charge transport in In$_2$O$_3$:PVA TFTs from ~4 cm$^2$/Vs (pristine In$_2$O$_3$) to ~0.6 cm$^2$/Vs with 6 wt. % PVA in the MO precursor solution (Fig. 6A and SI Appendix, Fig. S28) (52). Here, IZO:PVA and IGZO:PVA films were also fabricated to further probe the mechanism of PVA incorporation in IGO (SI Appendix, Fig. S39). As shown in Fig. 6B, in IZO:PVA (In:Zn = 7:3) TFTs, electron mobility monotonously falls as the PVA content increases from 0 to 10 wt. %, along with positively shifted $V_T$. Based on the XPS analysis of IGO:PVA and IZO:PVA films, it is clear that, in IGO:PVA films, high M–O–M content (>70%) is retained, even with 10 wt. % PVA (Fig. 1C). While in IZO, upon the addition of PVA, even though the remaining carbon content is similar (SI Appendix, Fig. S32), the M–O–M content drops considerably <70% (SI Appendix, Fig. S31), which will definitely erode electron transport. These data indicate that PVA-addition effects in MO systems without Ga can be quite different. Thus, to further probe the impact of different cations on MO introduction, IGZO:PVA films with two different metal compositions (In:Ga:Zn = 72.5:7.5:20 and 1:1:1) were fabricated and characterized in TFT geometries (SI Appendix, Figs. S33 and S34). As shown in Fig. 6C and D, while the mobility of IGZO(72.5:7.5:20) TFTs always decreases with increasing PVA content, for IGZO(1:1:1), the mobility first increases steeply from less than 10$^{-3}$ cm$^2$/Vs (0 wt. % PVA) to ~0.1 cm$^2$/Vs (4 wt. % ~8 wt. % PVA) and only then decreases. It is obvious that for the IGZO with less Ga (IGZO with In:Ga:Zn = 72.5:7.5:20), PVA does not promote carrier mobility and only enlarges $V_T$ (Fig. 6C), in contrast to the Ga-rich (In:Ga:Zn = 1:1:1) composition in which the mobility increases and $V_T$ is reduced (Fig. 6D). Thus, it is found that for solution-processed Ga-free and Ga-poor MOs, PVA is ineffective in enhancing charge transport vs. PVP, which depresses the electron mobility (27).

Note also that, compared with our previous work on other MO-polymer systems such as using polyethyleneimine (PEI) and PVP (52, 53), PVA contrasts in two important respects: 1) No similar to IGO:PVA, a very large increase in $I_{ON}$ among $I_{OFF}$ (In:Ga = 6:4) films with PVA incorporation is due to the following factors. As shown in the thermogravimetric analysis plots of SI Appendix, Fig. S39, the PVA thermolysis process is very different from that of Gly, with the latter compound being completely decomposed/vaporized below 200 °C, while PVA begins decomposition at ~250 °C, with the majority of the weight loss only occurring at ~300 °C. Note, however that PVA decomposition is far more efficient than that of PVP, where large amounts of PVP remain in the oxide film. As a result, the relatively slow decomposition speed of PVA may facilitate H diffusion to energetically stable sites in IGO, since the majority of the H in the films originate from the annealing atmosphere (SI Appendix, Fig. S15).

The present results, combined with the SS-NMR analysis and theoretical calculations, demonstrate that Ga in oxide semiconductors acts not only as an “oxygen getter,” due to large MO lattice-formation enthalpy (13), but also can readily change coordination number from six to four, particularly in the presence of PVA (SI Appendix, Table S11). These Ga coordinative transformations enable structural adjustments that help preserve the M–O–M network after PVA addition—in contrast to IZO, where Zn invariably remains four-coordinate (22, 54, 55). Moreover, Zn always corner-shares with neighboring polyhedra, whereas Ga prefers edge-sharing (55), which may help suppress void formation and maintain lattice density. Additionally, low-coordinate Ga, promoted by PVA incorporation, effectively increases the low-coordinated O content (SI Appendix, Fig. S22) that attracts H and enhances the electrical properties discussed above. Thus, PVA thermolysis facilitates the Ga six- to four-coordinate transition and places H at energetically adventitious sites. In addition, the H in such IGO:PVA films decreases the local distortion of all neighboring polyhedra, increases free carrier transport by providing more uniform conduction charge density, and also suppresses the localization of deep electron traps.

Conclusions

Semiconducting IGO:PVA films (In:Ga = 6:4, atomic ratio) can be grown by a low-temperature-solution process. At optimal PVA content, the mobility of IGO:PVA TFTs is enhanced from 0.10 cm$^2$/Vs (neat IGO) to >7 cm$^2$/Vs (8 wt. % PVA)—among the highest mobilities reported for solution-processed IGO films. Analysis of film microstructure, composition, and electronic structure, combined with MD/DFT simulations, attributes the PVA-enhanced TFT performance to H doping of IGO with the...
formation of OH groups, but not Ga–H bonds. Optimal amounts of H in IGO:PVA-derived films effectively suppress localized trap-site formation, reduce distortion of the metal coordination polyhedra, and afford far higher electron mobilities. Since achieving useful mobilities from solution-processed MO films with relatively high Ga content has presented a major scientific and technological challenge, the present approach circumvents the need to minimize Ga content and should be applicable to broad ranges of oxide electronics technologies.

**Materials and Methods**

**Precursor Preparation.** All chemicals were purchased from Sigma-Aldrich.* Exactly 354.8 mg of In(NO_3)_3·9H_2O, 297.2 mg of Zn(NO_3)_2·6H_2O, and 399.6 mg of Ga(NO_3)_3·xH_2O were dissolved in 10-mL portions of DI water. After complete metal nitrate dissolution, the solutions were mixed to obtain the desired In:Ga:Zn molar ratios. PVA (average M_w = 13,000 to 23,000, 98% hydrolyzed) was dissolved in DI water to a concentration of 8 mg/mL. Then, appropriate quantities of PVA solutions were added to the IGO precursor solutions to yield polymer:MO compositions from 0 to 14% by mass.

**Device Fabrication and Measurements.** For TFTs, n-type Si wafers with 300 nm of SiO_2 were used as gate electrodes and dielectrics, respectively. The Si wafer was first ultrasonically cleaned in an isopropanol alcohol bath for 20 min and then in an O plasma for 5 min. Then, the MO–polymer blend precursor was spin-coated on the Si/SiO_2 wafers at 3,000 rpm for 20 s and annealed at 300 °C for 30 min. This IGO:PVA spin-coating and annealing process was repeated thrice to achieve a film thickness of ~10 nm. Finally, 40-nm Al source-drain electrodes with a channel length (L) of 100 μm and channel width (W) of 1 mm were thermally evaporated at 5 × 10^-4 Pa. TFT electrical characterization utilized an Agilent B1500A semiconductor parameter analyzer. Ultraviolet-visible (UV-vis) spectra were acquired with a Thermo Scientific ESCALAB 250Xi at a base pressure of 2 × 10^-6 mBar. R-SoXS data at different energies across the carbon K-edge were collected with a Thermo Nicolet Nexus 870 spectrometer having a single-reflection horizontal ATR accessory with a diamond ATR crystal fixed on Thermo Scientific ESCALAB 250Xi at a base pressure of 2 × 10^-6 mBar, using the He I line at hν = 21.21 eV with samples biased at −5 V. All UV films were fabricated on indium tin oxide glass. EXAFS experiments were conducted at the BM3-D beamline at the Advanced Photon Source of Argonne National Laboratory. Ultraviolet-visible (UV-vis) spectra were acquired with a Perkin-Elmer LAMBDA 1050 instrument. For EXAFS and UV–vis measurements, all films were fabricated on quartz substrates. ToF-SIMS depth profiling was accomplished with a PHI TRIFT III instrument with Ar⁺ etching on a conducting Si wafer to avoid charging effects. FT-IR spectra were collected with a Thermo Nicolet Nexus 870 spectrometer having a single-reflection horizontal ATR accessory with a diamond ATR crystal fixed at a 45° incident angle. R-SoXS samples were prepared by using transparent SiN_x windows (Silson) as substrates, following the same spin-coating and annealing process (300 °C) to coat IGO:PVA films. The two-dimensional R-SoXS data at different energies across the carbon K-edge were collected at beamline 11.0.1.22 at the Advanced Light Source by using a Peltier-cooled (−45 °C) in vacuum (base pressure ~10⁻⁹ kPa [10⁻⁶ mBar]) and charge-coupled device detector (PI-MTE, Princeton Instruments; 2,048 × 2,048 pixels). The 1H MAS SS-NMR experiments were performed on a Bruker Avance-III 500 spectrometer with a 2.5-mm HX probe spinning at 25 kHz. All 1H MAS NMR spectra were acquired by using a spin-echo pulse sequence with a 90° pulse length of 2.7 μs and a recycle delay of 15 s. The background signals were collected under identical conditions with the empty rotor and were subtracted from the experimental data. The 1H chemical shift was calibrated with adamantane at δ = 1.8 ppm. To investigate the spatial proximity of Ga and H, 71Ga(1H) REDOR NMR was carried out on IGO:PVA powders. All 71Ga(1H) REDOR experiments were performed on a Bruker 830 NEO spectrometer at the 71Ga Larmor frequency of 253 MHz, spinning at 16 kHz using a home-built 3.2-mm probe. The 90° pulse lengths of 2 and 4 μs were employed for 71Ga and 1H, respectively. The 71Ga chemical shift was calibrated with Ga(NO_3)_3·6H_2O at δ = 0.0 ppm. The 115In MAS NMR spectra were collected by using a 3.2-mm home-built probe on a Bruker 830 NEO spectrometer operating at a Larmor frequency of 182.2 MHz. A frequency-stepped rotor-synchronized Quadrupolar Carr–Purcell–Meiboom–Gill pulse program was employed for acquisition at spinning rate of 16 kHz, with a 90° pulse length of 0.85 μs and recycle delay of 0.1 s to acquire the spectra. The resonant frequency was set at ±144 kHz from the carrier to excite the 115In resonances. Crystalline indium oxide was used as calibration standard at δ = 0.0 ppm. All NMR experiments were conducted at the National High Magnetic Field Laboratory.

**Theoretical Computations.** The amorphous In_2Ga_2ZnO_7 and In_2Ga_2ZnO_9 structures (In:Ga ~ 6:4 mol ratio) were obtained by using the ab initio MD liquid-quinque approach, as implemented in the Vienna Ab Initio Simulation Package. The calculations were based on DFT with periodic boundary conditions and employed the PBE functional within the projector augmented-wave method. For an accurate structural analysis of the simulated amorphous oxides, 300 K In–Ga–O structures were used. The electronic and optical properties of the DFT-optimized amorphous H-free and H-doped In–Ga–O structures were calculated by using the hybrid HSE approach with a mixing parameter of 0.25 and a screening parameter α of 0.2 Å⁻¹. Detailed discussion of the ab initio MD simulations and DFT calculations can be found in SI Appendix.

**Data Availability.** All data are available in the main text and SI Appendix.

**ACKNOWLEDGMENTS.** Thin-film oxide-polymer transistor fabrication, evaluation, and spectroscopy were supported by Air Force Office of Scientific Research Grant FA9550-18-1-0320 (to Y.C., G.W., and A.F.); the Northwestern University NSF Materials Research Science and Engineering Centers (MRSEC) Grant DMR-1720139 (to W.H., J.T., and L.Z.); US Department of Commerce, National Institute of Standards and Technology, and the State of Illinois; and Northwestern University NSF MRSEC Grant DMR-1720139 (to P.-H.C., S.P., and Y.-Y.H.). This work made use of the Center for Materials Design Award 70NANB19H005; and Flexterra Corp Grant DMR-1720139 (to Y.C., G.W., and A.F.); the Northwestern University NSF Materials Research Science and Engineering Centers (MRSEC) Grant DMR-1720139 (to W.H., J.T., and L.Z.); US Department of Commerce, National Institute of Standards and Technology, and the State of Florida; NSF Grant NSF/DMR-1644779; and Flexterra Corp Grant DMR-1720139 (to W.H., J.T., and L.Z.); US Department of Commerce, and Hybrid Nanotechnology Experimental Resource Grant ECCS-1542205, NSF Center for Hierarchical Materials Design Award 70NANB19H005; and Flexterra Corp (A.F.). SS-NMR was supported by the Northwestern University NSF MRSEC Grant DMR-1720139 (to Y.C., G.W., and A.F.), and the National High Magnetic Field Laboratory. The National High Magnetic Field Laboratory is supported by NSF Grant NSF/DMR-1644779 and the State of Florida. K.M. and J.E.M. were supported by NSF Designing Materials to Revolutionize and Engineer our Future Grant DMR-1729779 for MD simulations and DFT calculations; computational resources were provided by the NSF-supported Extreme Science and Engineering Discovery Environment program and by Department of Energy (DOE) National Energy Research Scientific Computing Center facilities. Scanning probe imaging (PSI) data were acquired at Beamline 11.0.1.2 of the Advanced Light Source (ALS), which is a DOE Office of Science User Facility under Contract DE-AC02-05CH11231. We thank C. Wang (ALS) for assisting with the R-SoXS experiment setup and providing instrument maintenance.

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