Photochemical Hydrogen Doping Induced Embedded Two-Dimensional Metallic Channel Formation in InGaZnO at Room Temperature

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Transparent conducting oxides (TCOs) are created by tuning the charge transport of wide bandgap oxides with the metallic ones, which are now playing a pivotal role in developing state-of-the-art functional devices as electrodes.1 Among various TCOs, InGaZnO (IGZO) has attracted a great attention as both in amorphous oxide semiconductor and TCO for the advanced transparent electronics with non-directional s-character electron conduction. Due to the excellent field-effect mobility (> 20 cm2/V sec) and large on/off current ratio (≈108), amorphous IGZO (a-IGZO) is currently being investigated as the advanced channel materials for thin-film transistor in flat panel display. a-IGZO, in similar to most metal oxides, has n-type doping characteristics owing to a native n-type donor—oxygen (O) vacancy and/or hydrogen.2,3 Initially, the O-vacancy defects exist as a lattice bond in single-crystalline and as surface and grain boundaries in polycrystalline metal-oxide film defects. They donate unsaturated (n - 1)d-electrons to the conduction band that consists of an ns empty orbital.2,4,5 However, since O-vacancy energy states are typically located in the bandgap, charge transport in metal oxides (particularly, in polycrystalline films) is mitigated by the trap-controlled hopping process. On further increasing O-vacancies or suboxide components to obtain high conductivity, the Fermi energy level (E_F) is

ABSTRACT The photochemical tunability of the charge-transport mechanism in metal-oxide semiconductors is of great interest since it may offer a facile but effective semiconductor-to-metal transition, which results from photochemically modified electronic structures for various oxide-based device applications. This might provide a feasible hydrogen (H)-radical doping to realize the effectively H-doped metal oxides, which has not been achieved by thermal and ion-implantation technique in a reliable and controllable way. In this study, we report a photochemical conversion of InGaZnO (IGZO) semiconductor to a transparent conductor via hydrogen doping to the local nanocrystallites formed at the IGZO/glass interface at room temperature. In contrast to thermal or ionic hydrogen doping, ultraviolet exposure of the IGZO surface promotes a photochemical reaction with H radical incorporation to surface metal—OH layer formation and bulk H-doping which acts as a tunable and stable highly doped n-type doping channel and turns IGZO to a transparent conductor. This results in the total conversion of carrier conduction property to the level of metallic conduction with sheet resistance of ≈16 Ω/□, room temperature Hall mobility of 11.8 cm2 V-1 sec-1, the carrier concentration at ≈1020 cm-3 without any loss of optical transparency. We demonstrated successful applications of photochemically highly n-doped metal oxide via optical dose control to transparent conductor with excellent chemical and optical doping stability.

KEYWORDS: IGZO · hydrogen doping · photochemistry · 2DEG · metallic conduction

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Hydrogen is also considered a native donor in a-IGZO. As there have been discussions on what may be the intrinsic n-type donor in ZnO, i.e., either an O-vacancy or H which might be supplied from the ambient water dissociation on O-vacancy site,8 the role of H as n-type donors in a-IGZO also has been proposed to lead to high or degenerated n-type doping as forming OH bond, thereby placing the $E_F$ level inside the conduction band.8,10,12,13 This is entirely different from O-vacancy doping, and the property of H-doped a-IGZO is ideal for creating TCO by modifying electronic band structures of the metal oxides for a conductivity boost-up, while simultaneously increasing visible transparency. Incorporation of H and O-vacancy into a-IGZO to increase the carrier density has been achieved by various methods such as O/H content control in deposition14 and post-treatment by H-ion implantation.13 However, O-vacancy doping in a-IGZO is subject to the inherent chemical/optical/electrical instability due to the dangling bond,15 and thermally formed H/OH groups have been occasionally reported as chemically unstable (therefore, mainly considered as environmental effect leading to a-IGZO instability) and also challenging for the facile control of H-dose.13 A reproducible, tunable, and chemically stable H-doping in metal oxides is yet to be developed, and it remains a crucial challenge in integrating H-doped metal oxides in advanced oxide-based devices while differentiating from the uncontrolled H-containing water effect.

In this study, we demonstrate that nonthermal UV photochemistry in air can be an effective method to functionalize the complex oxide (IGZO) surface and bulk with reactive H radicals formed by UV-induced adsorbed water dissociation acting as local n-type donors. Incorporation of H into IGZO led to the OH-rich near-surface region and H-doped nanocrystallites region offering a locally degenerate n-doped embedded conduction channel, showing a sheet resistance of $\sim 16 \ \Omega/\square$, room temperature Hall mobility of 11.8 cm$^2$ V$^{-1}$ sec$^{-1}$, the carrier concentration at $\sim 10^{20}$ cm$^{-3}$; this is equivalent to an insulator-to-metal conversion with excellent optical/chemical doping stability. This finding offers a facile but great controllability of H-doping to achieve a wide range of IGZO conduction from the improved semiconducting to metallic conduction.

RESULTS AND DISCUSSION

UV Exposure of a-IGZO. Figure 1a describes the experimental setup. A 50 nm IGZO layer was deposited onto a glass substrate via radio frequency sputtering. Two different UV lights (wavelengths of 185 and 254 nm at an illumination power of 28.7 mW/cm$^2$) were exposed onto the IGZO surface in air for up to 400 J/cm$^2$ (4 h exposure). Each UV dose was then calculated by multiplying the illumination power with exposure time. UV exposure supplies atomic O, H, and OH species formed through photodissociation of O$_2$ and H$_2$O molecules in air.16 When IGZO is grown at room temperature, it has typically an amorphous phase, as shown in the X-ray diffraction results (XRD, Figure 1b) and maintains the amorphous structure even after UV/air exposure. However, it was found from TEM analysis that the amorphous layer contains nanocrystals localized at the interface region of glass substrate (discussed later). The overall sizes of nanocrystals range from 3–5 nm, equivalent to XRD-amorphous. XRD and TEM results confirm that UV exposure did not induce any further crystallization of IGZO, which typically occurs with thermal annealing at $> 600^\circ$C.17 Based on Rutherford backscattering (RBS) analysis, the mean stoichiometry of the as-deposited IGZO bulk is $\text{In}_{0.65}\text{Ga}_{0.75}\text{Zn}_{0.53}\text{O}_{2.45}$, which is similar to the ideal stoichiometry of InGaZnO$_4$ (RBS data, Supporting Information (SI), Section 1). Rotating compensator-enhanced spectroscopic ellipsometry (SE) results give a precise optical bandgap (equivalent to the conduction band minimum, CBM) of IGZO at 3.4 eV by the Tauc plot of the absorption coefficient spectrum (Figure 1c and the inset) (see SI Section 2 for details on the SE analysis and modeling).

Physical Properties of UV-Exposed IGZO. Following dose-controlled UV exposure, electrical evaluations of UV-exposed IGZO layers were performed on the resistors using Mo metal-contact pads (Figure 2) (SI Section 3 provides device-fabrication details). UV/air exposure on the IGZO channels showed an extreme decrease in room temperature sheet resistance. At 100 J/cm$^2$ of UV dose, the sheet resistance dropped from $10^{12}$ to $10^3 \ \Omega/\square$ (by 9 orders of magnitude), which is equivalent to electrical conduction changing from insulating to metallic. Upon converting the sheet resistance to the specific resistivity for the entire channel thickness, 50 nm for UV/air-exposed IGZO (denoted as $\rho$) is considered, it dropped from $10^9$ to mid-$10^{-2}$ $\Omega\cdot$cm.

For a further reduction in sheet resistance, UV dose was increased up to 400 J/cm$^2$; however, it was not further enhanced and saturated. From Hall measurement analysis, the sheet charge concentration and Hall mobility at room temperature by 400 J/cm$^2$ of UV dose were respectively changed to $-4 \times 10^{13}$ cm$^{-2}$ and 11.8 cm$^2$ V$^{-1}$ sec$^{-1}$ from $-4 \times 10^{10}$ cm$^{-2}$ and $<1$ cm$^2$ V$^{-1}$ sec$^{-1}$ (below the Hall-detection limit) for the as-deposited. Therefore, all transport characteristics such as the sheet resistance, charge density, and mobility were dramatically altered as a result of UV/air exposure. The inset of Figure 2a shows conductance values of thickness varied IGZO films with UV/air exposure (SI Section 4 provides raw I–V curves). The insulator-to-metal conversion occurred only at the shallow regime not thicker than 70 nm. The best sheet
resistance was found at ∼16 Ω for 30 nm-thick IGZO. This result implies that UV/air induced conversion of IGZO to the TCO is due to the local properties and spatially limited by thickness constraint. The temperature ($T$)-dependent conductivities for the as-deposited and UV-exposed IGZO (400 J/cm² of UV dose) were significantly different. The inset of Figure 2b shows the activation energy ($E_a$ in eV) calculated from $T$-varied conductivity; it was 0.04–0.2 eV for the as-deposited sample, which is indicative of thermally activated carrier conduction. However, this value was very weakly positive (10⁻³–10⁻⁴ eV) or even negative (−10⁻³ eV) for the UV-exposed IGZO, indicating an irregular charge conduction in the oxide but rather metallic-like transport. This $T$-varied $I–V$ result is very similar to the previous data for IGZO both with the low and the high carrier density at 10¹⁴–10²⁰ cm⁻³. All electrical properties of 30 nm thick IGZO with and without UV exposure were summarized in Table 1. As shown in Figure 2c,d, UV–vis absorption spectroscopy analysis indicated that UV exposure on IGZO did not induce any marked change in the optical bandgap and transmission in visible range. Typical TCOs exhibit a trade-off between resistivity reduction and transparency degradation. Indeed, regarding the heavy doping effect in TCO such as free-carrier absorption or metallic reflection in near-infrared (NIR) region, the NIR transmission (in the inset of Figure 2c) is slightly reduced at several % but the noticeable blue bandgap shift (i.e., Murstein–Moss effect) in the visible region was not observed for UV/air-exposed IGZO compared to the as-deposited. No reduction of visible transparency and weak NIR absorption for the doped IGZO might be due to (1) the local doped region (or localized high carrier density and drift) and also (2) the modified electronic structure not to affect the optical transparency. Therefore, combined electrical and optical results suggest the potential to use UV/air-exposed IGZO as TCO material, because it displays excellent visible optical-stress stability and no visible range photocurrent; a significant challenge in IGZO applications to the flat panel display since photoinduced charges are subject to trapping/detrapping at defect states (SI Section 5 provides optical stability result for IGZO).

Photochemical Surface Chemical/Electronic Modification. Extensive XPS analyses were performed to investigate UV-assisted IGZO chemistry. Figure 3a shows narrow XPS scan spectra of O 1s and Zn 2p₃/₂ chemical binding states in the as-deposited and UV-exposed IGZO. In the O 1s XPS spectrum, two chemical binding states were
resolved: (1) O—metal (530.5 eV) and (2) OH—M (532 eV) binding states (where, M represents In, Ga, and Zn); these binding states agree with those reported in many previous reports.12,19 For Zn ions, three types of binding states were observed: (1) O-deficient Zn$^{1+}$ (1020 eV); (2) Zn$^{2+}$ in its full oxidation state (1021.7 eV); and (3) Zn—OH-related binding states (1022.8 and 1023.9 eV). In and Ga ions were found to display the identical O- and OH-related binding states (see SI Section 6 for In 3d and Ga 2p XPS spectra). UV-exposed IGZO surfaces showed remarkable changes in the metal—OH states (as shown in Figure 3b), implying that the metal—OH bond fractions normalized to the total areal intensity in each metal ion increase with increase in UV exposure; this trend corresponds to an increase in the OH bond fraction in the O 1s XPS spectra corresponding to UV exposure. Based on the fact that abundant excited atomic O (O$^0$) is produced and accompanied by OH and H radicals in air under UV exposure, it was confirmed from the XPS results that the UV exposure led to photochemical metal—OH complex formation on the IGZO surface. In fact, the aforementioned OH-hydrophilic surface conversion mechanism has been proposed in literature because metal—OH bonds predominantly form on UV-induced metal-defect sites.8,20 In the UV/vacuum (at 10$^{-3}$ Torr) experiment, O desorption was found to increase O-deficient Zn$^{1+}$ states (see SI Section 7 for details). On the other hand, UV/air exposure decrease Zn$^{1+}$ state as shown Figure 3b. Therefore, H radical incorporation into O-vacancy site is a potential OH-passivation mechanism by UV-induced O desorption ($i.e.$, the Zn—OH bond at 1022.8 eV). In addition, OH bond formation to regular Zn—O local bonds also potentially causes the formation of a higher metal oxidation state such as Zn—O—OH (at 1023.9 eV).

**TABLE 1. Summary on Measured Electrical Properties of 30 nm Thick IGZO with and without 400 J/cm$^2$ of UV Dose**

<table>
<thead>
<tr>
<th>UV dose (J/cm$^2$)</th>
<th>$R_{\text{sheet}}$ (Ω/□)</th>
<th>$n$ (cm$^{-2}$)</th>
<th>$\mu$ (cm$^2$/V·sec)</th>
<th>$E_A$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$10^{12}$</td>
<td>$\sim10^{10}$</td>
<td>&lt;1</td>
<td>0.04—0.2</td>
</tr>
<tr>
<td>400</td>
<td>16</td>
<td>$10^{13}$</td>
<td>11.8</td>
<td>$10^{-3}$</td>
</tr>
</tbody>
</table>

Figure 2. Conversion of the electrical property from insulator to conductor and quasi-metallic two-dimensional electron transport of UV/air-exposed IGZO TFTs. (a) IGZO sheet resistance ($R_{\text{sheet}}$) and specific resistivity (normalized to the film thickness) taken at room temperature as a function of UV/air exposure energy. The inset figure is the conductance and scaling factor (IGZO thickness normalized to 10 nm) change versus IGZO thickness at 10—200 nm. (b) Temperature-dependent sheet resistance plot. The inset figure shows the activation energy ($E_A$) in eV calculated from temperature-dependent conductivity. The slightly negative slope indicates that the thermal hopping conduction mechanism is not valid for a UV/air-exposed IGZO. The $R_{\text{sheet}}$ of as-deposited IGZO was recalculated from raw values by considering 10$^3$ times lower interfacial contact resistance of IGZO/Mo pad in vacuum condition for $T$-varied $I$–$V$ analysis compared to air ambient condition. This contact resistance lowering is related to some weakly bound O desorption effect at the top as-dep IGZO surface in vacuum which only affects the interfacial contact resistance (not applied for UV-exposed IGZO due to strong OH passivation at the surface). (c) Optical transmission and (d) absorption spectra for the as-deposited and UV/air-exposed IGZOs, respectively. The inset figure in (c) shows the NIR transmission spectra for the as-deposited and UV/air-exposed IGZO. There is a slight reduction of NIR transmission in UV-exposed IGZO, the indicative of carrier density increase in metal oxide TCO but no bandgap blue-shift.
Typically, a bulk metal hydroxide is more insulating than the metal oxide because of its large bandgap. For example, Zn–OH nanostructure can be synthesized via a colloidal method, and its bandgap is $\sim 0.8$ eV greater than ZnO since H bond forms the higher-lying H 1s molecular orbital state in ZnO and in Zn(OH)$_x$ ($x$:1/2–2) phase, this H-donor state becomes new intrinsic CB edge state, which defines the larger bandgap of Zn(OH)$_x$ than that of ZnO by 0.5–1 eV.8,21 Therefore, in order to investigate the spatial extension of hydroxide and its band electronic structure at the surface in a relation to the conductivity increase, we carried out angle-resolved XPS (AR-XPS) analysis, which is a unique nondestructive analytical method to examine surface binding state evolution depending on the sample depth. Figure 4a shows the OH fraction of Zn 2p and O 1s in the depth obtained from AR-XPS (SI Section 4 provides raw AR-XPS data). Using various tilt angles, the inelastic mean free path ($\lambda_{IMFP}$) was estimated at a corresponding photoelectron kinetic energy from the NIST electron effective-attenuation-length database.22 In the Zn 2p and O 1s spectra, the OH-related bond fraction was found to be higher in all cases in the UV-exposed IGZO within a depth of 1.2–2 nm compared to the as-deposited sample, and the absolute level of OH showed a systematic increase with UV exposure time; this suggests that a regular gas–solid diffusion process was achieved by controlling the UV dose. Because this diffusion process is equivalent to the infinite gas-source-diffusion process, a Gaussian profile was applied to fit the depth profile.23 The Zn 2p depth profile showed that OH-rich local regions extend to $\sim 1.5$ nm depth (the cross-point B) or to $\sim 0.9$ nm depth (cross-point A) (Figure 4a). In the Zn 2p-depth profile, the OH depth fraction was clearly limited to $<1.5$ nm even with a prolonged UV exposure time; however, an increase in the overall OH fraction was seen only in the confined OH-rich region. The O 1s depth profile reflects all metal–OH bond fractions and indicates that the OH-rich local region extends up to $<2.5$ nm for all metal–OH bonds. Therefore, UV/air exposure generates an ultrathin nanoscale OH–metal complex surface layer in the IGZO layer, which is typically formed only at the limited top surface. More importantly, this surface chemical change also generated valence band (VB) edge electronic states in the IGZO surface. Figures 4b shows the VB edge states of IGZO obtained using ultraviolet photoelectron spectroscopy (UPS) and XPS measurements, respectively. At different depths, namely $\sim 0.5$ (UPS) and $\sim 3$ nm (XPS), the VB edge and Zn 3d (at $\sim 9$ eV) states were all positively shifted and modified due to metal–OH mixed molecular orbital (MO) formation. Correspondingly, in the inverse photoemission spectroscopy (IPES) spectra, the major onset of empty state at the surface is about $+1.3$ eV shifted and features at about 6 and 8 eV of energy above $E_F$ level (at 0 eV) markedly increased in similar to the change in the feature at 7–8 eV of binding energy in
the UPS spectrum for the UV-exposed IGZO. Therefore, it is obvious that empty states in CB at IGZO surface are also significantly modified as a result of OH bond formation as well as occupied states in VB. Based on all measured, depth-resolved VBM values, the E_F level, and the surface bandgap energy, it is certain that surface chemistry and electronic structure of IGZO are converted to those in OH-functionalized IGZO by UV exposure with the large bandgap increase by up to $\sim 2$ eV at the top surface.

**Embedded Metallic Channel at the Interface.** Although XPS result can give a clear evidence of H-incorporation into IGZO surface, the origin of metallic conduction in IGZO is still vague since (1) the surface hydroxide revealed the large bandgap, reflecting the intrinsic insulating property, and (2) UV doping of IGZO shows strong substrate dependence; only IGZO on glass substrate shows a considerable increase in conductivity while on quartz and SiO_2/Si substrate, the degree of conductivity increase is limited at the order of $10^5$ to $10^6$ at room temperature (SI Section 8 provides dependence of conductivity on the substrate type). Moreover, the hydroxide surface chemistry of UV-exposed IGZO was detected for all substrate types. If the H-induced electronic structure modification of IGZO is the physical origin to create the surface metallic channel, it should have no substrate dependence. This implies the possibility of local channel formation in the film bulk; therefore, we performed cross-section high-resolution TEM-EELS analysis. Figure 5a,b shows TEM cross-sectional images and O K edge STEM-EELS spectra for the selected local spots along the film depth for the
as-deposited and UV-exposed IGZO. Surprisingly, it is found that the actual IGZO film consists of two distinctive morphological layers upon the film deposition; top amorphous and bottom nanocrystalline layers. All weak diffraction spots in SAED pattern, crystalline fringe in the images, and spot EDS data (see SI section 9 for EDS data) clearly confirm that nanocrystalline IGZO (nc-IGZO) is present but encapsulated by SiO$_2$ background. Since IGZO has been known as the native amorphous layer by sputtering deposition at room temperature, this is an unusual case but based on the mixed phase properties of nc-IGZO and SiO$_2$, the interfacial effect is considered to invoke room temperature nanocrystallization of IGZO. The glass substrate (soda-lime glass) used here contains various additives such as Na$_2$O, CaO, MgO, Al$_2$O$_3$, K$_2$O, etc. Among them, alkali ions such as Na, Ca, and K are occasionally reported as additives to promote crystallization of host material; from the spot STEM-EDS data, Ca was detected in IGZO with local variation of concentration (higher near the glass substrate than the middle of film). This is also supported from TEM analysis for IGZO film on silicon and quartz substrates showing that the entire film consists of single amorphous phase of IGZO without nanocrystallites and mixed phases (see SI section 8). This suggests a stronger relation of morphological substrate effect in the film bulk to physiochemical origin for insulator-to-metal transition by H-doping than the surface chemistry change. Interestingly, Ca-doping in IGZO was also reported to show dramatic improvement in transistor characteristics. Ca was claimed to promote IGZO reduction to increase carrier density. In this study, Ca might act as the promoter for the effective H-incorporation to the locally reduced IGZO in the vicinity of glass substrate. Furthermore, the lowermost nc-IGZO region has the largest nc size and continuous arrangement among nanocrystallites acting as the nanoscale (<5 nm) conduction channel, but as being more distant from the glass substrate, the nc size becomes smaller in coincidence to the profile of Ca content. From O K$_1$ EELS spectra in Figure 5b, the O-vacancy associated substate (denoted as $E_D$) disappeared after UV exposure. The spectral error deviation in EELS spectra is ±0.1 eV. In SIMS depth profile, the change in H is resolved only at the nc-IGZO region, which may be related to the degree of local H-doping activation.
The time-of-flight secondary ion mass spectrometry (TOF-SIMS) depth profile in Figure 5c suggests that H content, though exact chemical binding states are unknown, is relatively higher at the bottom nc-IGZO region but no much increase in total amount over the entire film after UV exposure. This serves as the evidence supporting the fact that the fast diffusive UV-generated H leads to H-dopant activation at nc-IGZO region across 50 nm thick IGZO film. As the IGZO film becomes thicker, H-activation in the nc-IGZO region is hindered due to the thick portion of amorphous layer since the nc-IGZO layer is typically localized at the similar thickness at the interface with the glass substrate (as shown in I–V result at the inset of Figure 2a). This is confirmed by the cross-sectional TEM images for 100 nm thick IGZO, where the bottom 20–30 nm thick nc-IGZO region is localized at the glass/IGZO interface, but the other region consists of 70–80 nm thick a-IGZO (see SI 10 for TEM images). It is noted that the as-deposited IGZO initially contains a high level of H content, which is at the similar level to that in the UV/air exposed IGZO, but the chemical state between two samples should be very different each other; i.e., H exists as a physisorbed water and functional OH group inside the as-deposited not as electronically activated H donor.

As clearly shown in the chemical analysis, reactive H radicals supplied by UV-induced water dissociation react with IGZO surface. From the previous theoretical calculation, it was suggested that H incorporation into IGZO typically results in OH bond formation. The electrical effect of OH adsorbed on surfaces in metal oxides is various: it can act as both donor and acceptor depending on the material. However, OH formation resulted from H doping in IGZO donates electron; i.e., acts as n-type donor though the reaction; H\(^+\) (from UV dissociation) + O\(^{-}\) (in IGZO) $\rightarrow$ OH\(^-\) (in IGZO) + e\(^-\). Thereby, the ions in the IGZO reacting with H\(^+\) are converted to O\(^{2-}\)-H\(^+\). This requires extra negative charges or electrons to keep the charge neutrality and therefore explains the increase of electron density by H incorporation leading to OH bonding formation in IGZO. This effect is also confirmed in ZnO. The TOF-SIMS depth profile also indicates the extended region with the higher concentration of H even than In, Ga, and Zn metal ions is consistent to metal hydroxide formation in the surface region (the inset of Figure 5). Therefore, it is inferred from this study that local bonding environment of metal–oxygen can lead to different H bonding states; either hydroxide dominant in O-rich condition (at the surface) or H-doping dominant in O-poor condition (at the bulk). Especially, the reactive site of H donor in the nc-IGZO region is most probably O-vacancy associated defects. Based on the relatively weak improvement of carrier conduction in H-doped IGZO on SiO\(_2\)/Si and quartz substrates having the same surface chemistry with IGZO on the glass is regarded due to (1) the weak H-doping activation in the amorphous phase and (2) low degree of H dopant activation in absence of nanocrystallites (see SI Section 8 for TOF-SIMS data). It is concluded that the active H-doping activation and high carrier mobility require the presence of nc-IGZO. Definitively, the photoinduced carriers are generated under UV light exposure and lead to the persistent photoconductivity\(^{26}\) in IGZO, and this occasionally leads to the photoinstability of IGZO TFTs. However, this case is confirmed as the permanent chemical doping effect which persisted permanently (see SI Section 11 for 1 year doping stability test). In addition, the excellent air-aging stability (at <1% conductance deviation) over 1 year of conductive H-doped IGZO with Al\(_2\)O\(_3\) passivation layer capping was achieved, and the spatial doping uniformity (at <10% conductance deviation) at the scale up to 4 in. wafer equivalent size was also confirmed (see SI Section 5A for doping stability and uniformity test). The adjusted UV-assisted OH-doping dose (i.e., UV time and power adjustment) was found to modify band electronic structures and electrical properties of IGZO while maintaining semiconducting properties while improving TFT performance (see SI Section 11 for all TFT results).

**CONCLUSION**

We demonstrate that nonthermal UV photochemistry in air can be an effective method to functionalize the complex oxide (IGZO) surface with reactive H radicals formed by UV-induced adsorbed water dissociation acting as local n-type donors. A remarkable feature in this photochemical doping scheme is thus creation of a two-dimensional local metallic nc-IGZO channel by incorporating H donor in the controllable way to adjust the doping dose with excellent optical and chemical doping stability ideal for flexible device and display applications. Furthermore, the ongoing research suggests an extension of this finding to new aspects that this photochemical H-doping can be a generic doping method for other metal oxides and can be utilized for lithographically patterned doping of a metal oxide film at various conductivity levels for diverse device applications.

**METHODS**

**Growth of a-IGZO Layer Using RF Sputtering.** A 50 nm a-IGZO layer was deposited onto a 150 nm-thick SiO\(_2\) on Si or glass substrate via RF sputtering at an RF power of 40 W at room temperature and a process pressure of 5 mTorr in a mixture of 9:1 Ar/O\(_2\).

**UV Exposure on a-IGZO Layer.** For UV exposure, the a-IGZO top surface was steadily exposed by two UV photons (wavelengths of 185 and 254 nm) at an illumination power of 28.7 mW/cm\(^2\) from 1 (optical dose at 100 J/cm\(^2\)) to 4 h (optical dose at 400 J/cm\(^2\)) at room temperature either in air or in vacuum.
Finally, the atomic composition of IGZO thin films was analyzed using RBS (65DH-2 equipped with a He source (2 MeV)) and TOF-SIMS with Cs⁺ at 1–9 keV of ion energy.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b05342.

RBS data; SE analysis; details of IGZO TFT/resistor device; stability/uniformity test; thickness-dependent doping effect; additional XPS spectra; UV/vacuum exposure results; doping dependence on substrate types; TEM-EDS analysis; TEM images of IGZO films with a thickness of 100 nm; characteristics of the TFT devices with UV-treated IGZO semiconductor channels (PDPh).

Note Added after ASAP Publication: The version of this paper that was published October 1, 2015, contained errors in Figure 2. The corrected version was reuploaded October 6, 2015.

REFERENCES AND NOTES