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Permanent optical doping of amorphous metal oxide semiconductors by deep ultraviolet irradiation at room temperature

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We report an investigation of two photon ultraviolet (UV) irradiation induced permanent n-type doping of amorphous InGaZnO (a-IGZO) at room temperature. The photoinduced excess electrons were donated to change the Fermi-level to a conduction band edge under the UV irradiation, owing to the hole scavenging process at the oxide interface. The use of optically n-doped a-IGZO channel increased the carrier density to ~10^{18} cm^{-3} from the background level of 10^{16} cm^{-3}, as well as the comprehensive enhancement upon UV irradiation of a-IGZO thin film transistor parameters, such as an on-off current ratio at ~10^8 and field-effect mobility at 22.7 cm^2/V s. © 2010 American Institute of Physics. [doi:10.1063/1.3429586]

The application of transparent metal-oxide semiconductors (TMOSs) to a semiconducting nanoscale channel of emerging electronic devices (e.g., transparent thin film transistor or TFT) has had many beneficial effects, such as mobility enhancement and increased functionality of electronic devices. One of the key techniques needed to extend the application of TMOSs to the channel of functional devices would be control on intrinsic doping manipulation at room temperature. Most of the transparent metal-oxide thin films have shown n-type intrinsic doping properties that can contribute electrons for conduction. However, doping manipulation of n-type transparent metal oxides, in most cases, is challenging because the nature of n-type doping in the transparent elemental metal oxides (e.g., ZnO and TiO_2) of interest stems from native defect-associated donors. Many physically insightful studies on the origin of native doping mechanisms have proposed the presence of native donors, such as oxygen vacancies and metal interstitials.

The intrinsic n-type doping of TMOS is typically subject to material structure-driven defect chemistry and physical distribution, which cannot be controlled as an independent property. In addition, defect formation can be detrimental to the further enhancement of electron mobility since the defect-associated traps result in not only limited charge transport but also device performance degradation through charge trapping during circuit operation, which causes critical problems in the reliability of transparent electronics under both voltage stress and photoeffect. Therefore, nonthermal doping of TMOS without the intrinsic property degradation should be a greatly interesting topic.

In this investigation, the subject of study was ultraviolet (UV) irradiation induced permanent n-type doping level manipulation of a-IGZO for room temperature (RT)-processed TFT channel application. The photo-induced excess electrons were donated to change the Fermi-level to a conduction band edge under the UV irradiation, owing to the hole scavenging process at the oxide interface. The optically n-doped a-IGZO channel achieved the increase of carrier density to ~10^{18} cm^{-3} from the background level of 10^{16} cm^{-3}, as well as the comprehensive enhancement upon UV irradiation of a-IGZO thin film transistor parameters, such as an on-off current ratio at ~10^8 and field-effect mobility at 22.7 cm^2/V s.

The 100 nm Mo layer used as a gate electrode was deposited on the glass substrate by direct current sputtering at 80 W of radio frequency (rf) power and 5 mTorr Ar gas conditions and patterned by the lithography and etching process. The 150 nm SiO_2 layer used as a gate insulator was then deposited by plasma enhanced chemical vapor deposition. The 50 nm a-IGZO channel layer was deposited by rf-sputtering at 40 W of rf power and 5 mTorr of process pressure in a mixture of 9:1 Ar/O_2 and subsequently patterned by lithography and wet-etching, using a buffered oxide etch solution. The 100 nm Mo layer for source and drain contact was deposited with the same method used for gate electrode deposition and patterned by lift-off method to prevent surface damage to a-IGZO when exposed to the etching chemical solution for Mo. For UV irradiation, before forming source and drain Mo metal contacts, IGZO TFT stacks having a-IGZO as the top surface were steadily irradiated by two photon (wavelengths of 185 and 254 nm) deep UV light at 25 mW of illumination power from 30 to 120 min. The primary dimension of a-IGZO channel is the 50 μm length (L) × 40 μm width (W) but TFTs with several different L (20, 40, and 50 μm) × 40 μm W were fabricated to investigate the contact resistivity, channel resistivity, and charge concentration. The electrical characteristics of a-IGZO based TFT were measured by using current-voltage (I-V) analysis equipment (Agilent 5270B). The width and length of the channel were 40 μm and 50 μm, respectively, and the drain-source voltage (V_{ds}) is 5 V. With the...
The Tauc plot varied UV irradiation extracted from optical three-phase modeling from SE. The energy separation between $E_g$,opt and Fermi energy level is important as the threshold energy for the charge transport. Therefore, if the defect generation occurring in the VB. At the same time, those UV light photon energies for optical doping were high enough to UV-irradiated a-IGZO films on glass, respectively. The UV states from SE measurements and VB edge XPS spectra of a-IGZO with and without time-varied UV irradiation.

All IGZO thin films were investigated by x-ray diffraction (XRD) analysis (Rigaku DMAX PSPC MDG 2500) to confirm the amorphous phase. The CB edge states of a-IGZO thin films were analyzed from the absorption spectra taken by a rotating compensator enhanced spectroscopic ellipsometry (SE) measurement with a spectral resolution of 15 meV and three phase optical modeling.8 The VB edge of a-IGZO thin films was analyzed by XPS [Physical Electronics, PHI 5400 ESCA/XPS system equipped with an Al anode X-ray source (1486.6 eV)]. The energy resolution for each point is 0.05 eV. All the peak energy has been self-calibrated to C 1s and O 1s reference peak state.

Figures 1(a) and 1(b) show the $\varepsilon_2$ spectra of CB edge states from SE measurements and VB edge XPS spectra of UV-irradiated a-IGZO films on glass, respectively. The UV light photon energies for optical doping were high enough to excite electrons to deep CB states, leaving excess holes in the VB. At the same time, those UV light energies of 472 and 646 kJ/mol were also high enough to break Zn-O bonds (183 kJ/mol), which can result in oxygen vacancy defects. The design of optical doping using UV light irradiation resulted in excess electron generation without photoinduced defect subgap-state generation. This aspect of UV irradiation-induced defect generation was studied by SE analysis, because this technique has been well known to detect the oxide-defect-associated empty subgap states (i.e., oxygen vacancy) at the volume density $>10^{18}$ cm$^{-3}$, which is a threshold defect level to induce the trap-assisted hopping transport.9 Therefore, if the defect generation occurring in a-IGZO is significant enough to change the intrinsic charge transport mechanism, this should be detected by SE as a subgap state.

The optical band gap ($E_{g,\text{opt}}$) of all a-IGZO films extracted from Tauc plot of absorption spectra [the inset of Fig. 1(a)] was estimated at 3.4 ± 0.05 eV, which are similar to the reported values (3.2–3.4 eV) in the a-IGZO films deposited by sputtering deposition technique.10 The strong CB onset energy in $\varepsilon_2$ spectra is assigned as 3.7 eV. Notably, the energy separation between $E_{g,\text{opt}}$ and Fermi energy level is important as the threshold energy for the charge transport transition. Another crucial feature of the $\varepsilon_2$ spectra was the gap-state below 3.4 eV. In contrast to nanocrystalline ZnO thin films, which show strong localized defect states (at the density $>10^{18}$ cm$^{-3}$) near the CB edge,12 the absorption features of localized defect states as detected in the polycrystalline ZnO were hardly observed in $\varepsilon_2$ spectra for the as-deposited and UV-irradiated a-IGZO at any irradiation time. This implies the density of localized defect in a-IGZO is at about the detection limit (mid-10$^{13}$ cm$^{-3}$) of SE measurement. The weak gap-state at 1.5–3 eV was due to the optical absorption of the a-IGZO/glass interface, or equivalently, the interference reflection at the nonhomogenous layer between a-IGZO and glass.

XPS VB edge spectra for UV-irradiated a-IGZO in Fig. 1(b) revealed systematic Fermi energy level ($E_F$, or binding energy at 0 eV) rise against the VB onset edge toward the CB edge, from 2.9 ± 0.1 (as-deposited) to 3.6 ± 0.1 eV (120 min of UV irradiation). This rise of $E_F$ clearly suggests that a longer period of UV irradiation leads to more n-type doping of a-IGZO, eventually converting a-IGZO into a degenerated n-type semiconductor after 120 min of UV irradiation. From the carrier transport perspective, the $E_F$ level after 60 min of UV irradiation of a-IGZO was in the region of CB tail states (or $E_{g,\text{opt}}$ level at 3.4 eV), as shown in the $\varepsilon_2$ spectra. This clearly suggests that the transport mechanism changed from percolation to degenerated n-type conduction in accumulated a-IGZO surface channels with UV irradiation induced n-type doping. However, $E_F$ after 120 min of UV irradiation of a-IGZO was at the deep CB level (at 3.7 eV), so that bulk transport in a-IGZO was simply metallic, at a significant loss of semiconductor characteristics. A plausible origin of $E_F$ level change under UV irradiation is the fact that photoinduced charges having higher energy (approximately several electron volt) stemming from (i) excess UV photon energy well above the band gap and (ii) the built-in potential in a-IGZO could modify surface/near-surface electronic structure via the charge transfer at surface states.

FIG. 1. (Color online) (a) $\varepsilon_2$ spectra of a-IGZO with and without time-varied UV irradiation extracted from optical three-phase modeling from SE. The Tauc plot ($\alpha E^2$, where $\alpha$ is absorption coefficient and $E$ is photon energy) of absorption spectra for the as-deposited a-IGZO in the inset. (b) VB edge XPS spectra of a-IGZO with and without time-varied UV irradiation.

FIG. 2. (Color online) (a) a-IGZO TFT transfer characteristics ($I_{ds}$-$V_{ds}$) and output ($I_{ds}$-$V_{gs}$) characteristics in the inset. The $I_{ds}$-$V_{gs}$ plot confirms that a-IGZO TFTs were working in the typical enhanced FFT operation mode. (b) Plot of carrier concentration in the surface channel layer, n and field-effect mobility, $\mu_{FE}$ of TFTs against UV irradiation time.

XPS VB edge spectra for UV-irradiated a-IGZO in Fig. 1(b) revealed systematic Fermi energy level ($E_F$, or binding energy at 0 eV) rise against the VB onset edge toward the CB edge, from 2.9 ± 0.1 (as-deposited) to 3.6 ± 0.1 eV (120 min of UV irradiation). This rise of $E_F$ clearly suggests that a longer period of UV irradiation leads to more n-type doping of a-IGZO, eventually converting a-IGZO into a degenerated n-type semiconductor after 120 min of UV irradiation. From the carrier transport perspective, the $E_F$ level after 60 min of UV irradiation of a-IGZO was in the region of CB tail states (or $E_{g,\text{opt}}$ level at 3.4 eV), as shown in the $\varepsilon_2$ spectra. This clearly suggests that the transport mechanism changed from percolation to degenerated n-type conduction in accumulated a-IGZO surface channels with UV irradiation induced n-type doping. However, $E_F$ after 120 min of UV irradiation of a-IGZO was at the deep CB level (at 3.7 eV), so that bulk transport in a-IGZO was simply metallic, at a significant loss of semiconductor characteristics. A plausible origin of $E_F$ level change under UV irradiation is the fact that photoinduced charges having higher energy (approximately several electron volt) stemming from (i) excess UV photon energy well above the band gap and (ii) the built-in potential in a-IGZO could modify surface/near-surface electronic structure via the charge transfer at surface states.

Figures 2(a) and 2(b) represent the electrical data set of as-deposited and UV-irradiated a-IGZO TFTs. The analysis of the $I_{ds}$-$V_{gs}$ curve in Fig. 2(a) was surprising in that comprehensive TFT performances have been significantly enhanced with longer UV irradiation of up to 60 min; for ex-
ample, (i) on/off current ratio increase by two orders to $2.1 \times 10^5$, (ii) SS decrease to 0.25/decade, (iii) negative $V_{th}$ shift to 2.8 V, and (iv) $\mu_{FE}$ increase to 22.7 cm$^2$/V s. The $V_{th}$ for $I_{ds}-V_{gs}$ analysis was 5 V for all as-deposited and UV-irradiation TFTs. The origin of off-current increase at the negative $V_{th}$ has been identified as the gate leakage current from $I_{ds}-V_{gs}$ analysis under the open source contact.

In order to confirm whether this was a permanent optical doping effect or subject to the time-dependent slow recovery, the measurement was repeated six months later, and Fig. 2(a) compares the measurement at the time of fabrication to the repeated measurements six months afterwards, for the $I_{ds}-V_{gs}$ curves of the same TFT devices with 60 min of UV irradiation. This comparison of time-dependent $I_{ds}-V_{gs}$ reveals the strong long-term optical doping stability of a-IGZO TFTs. The slight negative $V_{th}$ shift for the aged TFT was due to the chemical aging effect commonly observed for aged TFTs without passivation layers. This optical doping was also confirmed to be stable at the elevated temperature based on $I_{ds}-V_{gs}$ results at 100 °C (not shown here).

In order to explain the principle of the effects of UV irradiation on n-type doping and $V_{th}$ shift for a-IGZO TFTs, a qualitative model is proposed in Fig. 3(a). The UV light excites electrons while creating holes in VB to the upper energy levels in CB. It is suggested that two photon (4.9 and 6.7 eV) UV irradiation far larger than the band gap energy can excite electrons (at the density of $10^{13}$ cm$^{-2}$s$^{-1}$) to deep CB levels with (i) different transition matrix elements and (ii) much higher photo-induced e-h pair density than single photon UV absorption. However, the more complete explanation for the photoexcitation mechanism of two photon UV irradiation is under investigation.

In Fig. 3(a), the built-in potential of a-IGZO/SiO$_2$ stacks caused asymmetric excess e-h separation, which created drift motion of holes toward the a-IGZO/SiO$_2$ interface and electrons to the opposite end of the a-IGZO surface (at the time scale of $< 10^{-11}$ s). The excess holes were then scavenged at the negatively charged interfacial defects which neutralized the interfacial oxide defects. Therefore, under equilibrium conditions (i.e., after thermal relaxation) with no light, the excess electrons survived in CB without direct recombination (at the time scale of $> 10^{-9}$ s) with the excess holes which had already been scavenged at the interfacial defects and donated as free charge carriers to a-IGZO. The overall effect was to make a-IGZO a more highly doped n-type semiconductor, the longer it was exposed to UV irradiation. The plots of flat band voltage ($V_{FB}$) shift and effectively trapped hole density ($N_{EFF, hole}$) from C-V analysis as a function of UV irradiation time.