Applied Physics Letters

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Cite as: Appl. Phys. Lett. **100**, 102110 (2012); https://doi.org/10.1063/1.3691920
Submitted: 16 December 2011 • Accepted: 15 February 2012 • Published Online: 08 March 2012

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The effects of organic material-treated SiO_2 dielectric surfaces on the electrical characteristics of inorganic amorphous In-Ga-Zn-O thin film transistors

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(Received 16 December 2011; accepted 15 February 2012; published online 8 March 2012)

We investigated the influence of organic dielectric surfaces on the electrical characteristics of inorganic amorphous indium-gallium-zinc oxide (a-IGZO)-based thin film transistors (TFTs). To modify the dielectric surface, various self-assembled monolayers and polymer thin films with different functional groups were introduced. Electrical measurements of the a-IGZO TFTs using surface-modified gate dielectrics revealed that the threshold voltages shifted toward positive values as the surface functional groups attract more electrons in the a-IGZO thin films. These results indicate that the channel conductance and carrier density of a-IGZO TFTs could be tuned by simple modification of the dielectric surfaces with organic materials. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3691920]

Amorphous indium-gallium-zinc oxides (a-IGZO) have emerged as representative of transparent oxide semiconductors in industry due to their high carrier mobility, low processing temperature, and compatibility with plastic substrates.[1,2] The a-IGZO-based thin-film transistors (TFTs) are considered to be the promising switching devices for use in the backplane circuits of transparent, flexible displays, or electronic paper.[3,4] For the purposes of demonstrating such electronic devices based on a-IGZO TFTs, polymers can be good material candidates as gate dielectric layers because of their high transparency and flexibility, low cost, easy processing from solution, and good insulating properties.[5–7] Prior to applying a polymer dielectric, in-depth studies of the compatibility between the a-IGZO and a polymer dielectric layer are needed. However, studies of the influence of an organic dielectric surface on the characteristics of an a-IGZO inorganic semiconductor have been largely unexplored in comparison to studies of organic semiconductors, such as pentacene, even though the dielectric-semiconductor interface plays an important role in the operation of TFTs.[8]

In general, for the practical applications of TFT devices, it is required that the device operation be controlled via carrier density modulation in the channel. In a-Si TFT technology, the channel carrier density is usually modulated via ion implantation-based doping methods that can potentially damage devices that include organic materials. Kobayashi *et al.* and Pernstich *et al.* established a simple and efficient method for modulating the charge carrier density by introducing surface dipoles onto dielectric surfaces. Manipulation of the dielectric surface dipole provides a good alternative to controlling the channel carrier density and, therefore, the operation of devices based on a-IGZO TFTs. This method particularly advances the realization of transparent flexible electronic devices using polymer gate dielectrics.

In this letter, we describe how a-IGZO-based TFTs perform when functionalized with a variety of organic dielectric surface. To modify a 300 nm thick SiO_2 gate dielectric surface, we introduced an organic thin layers onto the dielectric such as a self-assembled monolayer (SAM) and an insulating polymer having any of a variety of functional groups on the molecular ends, as shown in Fig. 1.[9–11] Ultraviolet photoemission spectroscopy (UPS) analysis was used to measure the relative direction and strength of the surface dipole formed in the presence of the functional groups on the SiO_2 dielectric surfaces. By measuring the electrical characteristics of the a-IGZO TFTs functionalized with various surface-modified gate dielectrics, the effects of the organic material-treated

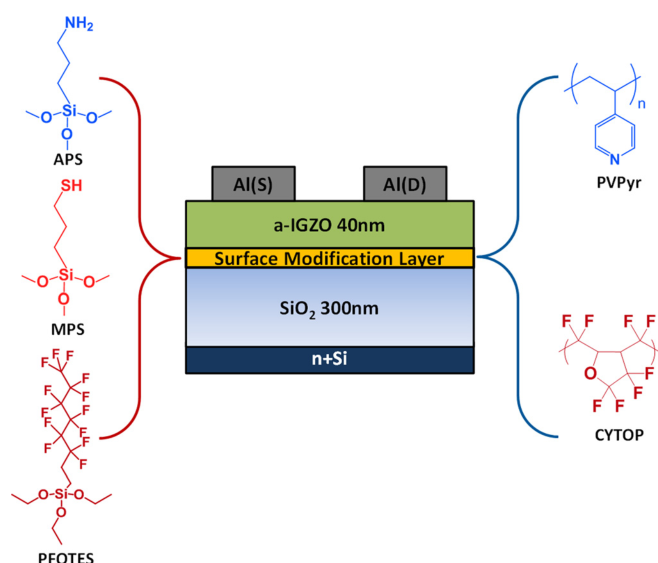

FIG. 1. (Color online) Chemical structures of the SAMs (left) and the polymer thin films (right) employed as surface modification layers in this study. (Blue color: electron donating, red color: electron withdrawing.) The device structure of a bottom-gated top-contact a-IGZO TFT used in this study (center).

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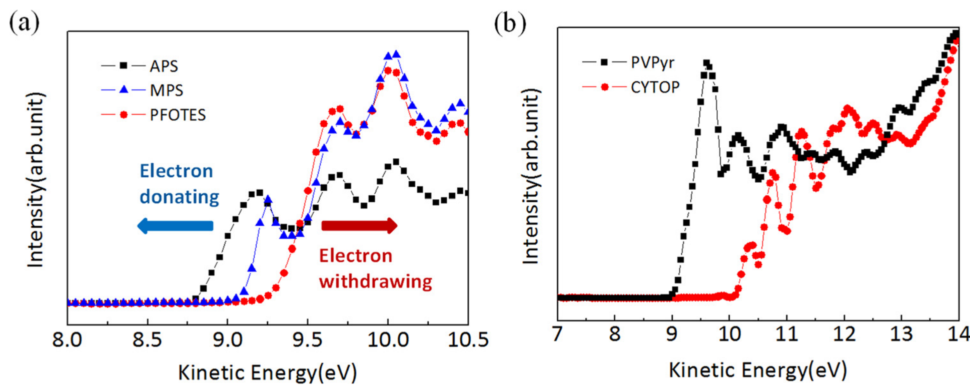

FIG. 2. (Color online) UPS spectra of the surface-modified gate dielectrics with (a) three SAMs and (b) two polymer thin films.

dielectric surfaces on the electrical characteristics of a-IGZO TFTs were investigated.

Three types of SAM material and two types of polymer with functional groups of varying electronegativity were used as surface modification layers. The left side of Fig. 1 shows the chemical structures of each SAM: aminopropyltriethoxysilane (APS, Aldrich, 99%), mercaptopropyltriethoxysilane (MPS, Aldrich, 95%), and perfluorooctyltriethoxysilane (PFOTES, Aldrich, 98%). The chemical structures of the polymers, poly-4-vinyl pyridine (PVPyr, Aldrich) and CYTOP (AGC), are shown in the right-hand side of Fig. 1.

Organosilane molecules, which have several functional groups of different electronegativity, are characterized by an electric dipole determined by the charge distribution within the molecule.[12] When these molecules closely pack to form a SAM, each molecule's electric dipole produces an overall net polarization inside the SAM and introduces a surface dipole at the interface between the semiconductor and the dielectric. A SAMs surface dipole modulates the energy level of the semiconductor at the interface.[10] UPS analysis was used to determine the relative direction and strength of the surface dipole of a SAM (i.e., the electron-withdrawing or -donating ability).[13] Figure 2(a) shows the UPS data for SiO_2 surfaces treated with each of the three SAMs. UPS equipment (Escalab 220IXL) was used along with the He(I) emission at 21.2 eV. Figure 2(a) shows that the highest onset point of secondary electrons was observed from the PFOTES SAM (9.3 eV), followed by the MPS SAM (9.0 eV) and the APS SAM (8.75 eV). PFOTES induces a partial negative charge at the a-IGZO interface, thereby shifting the surface potential toward higher electron energy levels. As a result, when a-IGZO is deposited on a PFOTES-treated dielectric surface, band bending toward higher energy levels of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the a-IGZO occurs at the nearest interface. PFOTES is, therefore, expected to decrease the electron carrier density in an a-IGZO in the channel region.[10,11] Similar behavior was observed in the MPS-treated samples, although the strength of the electron-withdrawing properties was lower than that of the PFOTES-treated surface. On the other hand, APS was expected to increase the electron carrier density of an a-IGZO TFT in the channel region because its surface dipole direction is opposite that of PFOTES. This property lowers the LUMO and HOMO level of a-IGZO and leads to electron accumulation.[10,11] The energy level difference of the a-IGZO between on the dielectric treated with PFOTES and APS was expected to be 0.55 eV based on UPS analysis.

Polymer thin films coated onto SiO_2 dielectrics can modulate the interface energy levels between the semiconductor and the dielectric, similar to SAMs.[8] To modify the surface dipole characteristics of the gate dielectrics with maintaining bulk properties (such as leakage currents and capacitances), the polymer thin-films were controlled to have an ultra-thin film thickness. The thicknesses of the ultra-thin polymer films were characterized by using an ellipsometer (J. A. Woollam. Co., Inc.) and found to be 12.2 ± 0.3 nm (for CYTOP) and 10.8 ± 0.3 nm (for PVPyr), respectively. UPS data for polymer thin film-coated SiO_2 dielectrics are plotted in Fig. 2(b), showing a trend analogous to that observed for the SAM-treated samples. A higher onset point was observed for the CYTOP-coated dielectric (10.11 eV) than for the PVPyr-coated dielectric (9.0 eV). The UPS data associated with the SAM-treated and polymer-coated samples indicated that PFOTES and CYTOP-modified dielectric surfaces would be more highly electron-withdrawing in an a-IGZO than the APS- or PVPyr-modified dielectric surfaces.

Atomic force microscopy (AFM, characterized using a Multimode SPM, Digital Instruments) topographs of a-IGZO films deposited on various dielectric surfaces are shown in Fig. 3(a). These images show that all a-IGZO films had similar morphologies with a 5–9 Å r.m.s. roughness (R_q), regardless of the dielectric surface dipole difference. Figure 3(b) shows a scanning electron microscopy (SEM) image and corresponding energy dispersive spectrometry (EDS) images of Zn, Ga, and In atoms of a-IGZO films deposited on the polymer-coated (PVPyr) SiO_2 dielectrics. As shown in the SEM image, there are no aggregates or crystallites throughout the film. Moreover, the distribution of Zn, Ga, and In atoms is uniform, which implies the IGZO films are not crystalline. The SEM and EDS results of the a-IGZO film deposited on SAM-treated (PFOTES) dielectrics are almost identical with Fig. 3(b) (data not shown). Also, the θ-2θ mode out-of-plane x-ray diffraction (XRD) profiles of the a-IGZO films deposited on the various dielectric surfaces, as plotted in Figs. 3(c) and 3(d), revealed that all a-IGZO films had amorphous structures because they showed no peaks over the range 20°–40° (considering that the IGZO crystals showed a sharp peak at 32°).[14] The AFM, SEM, EDS, and XRD results suggest that the morphology and crystalline structure of the a-IGZO films were not significantly affected by the organic dielectric surface, in contrast to the behavior

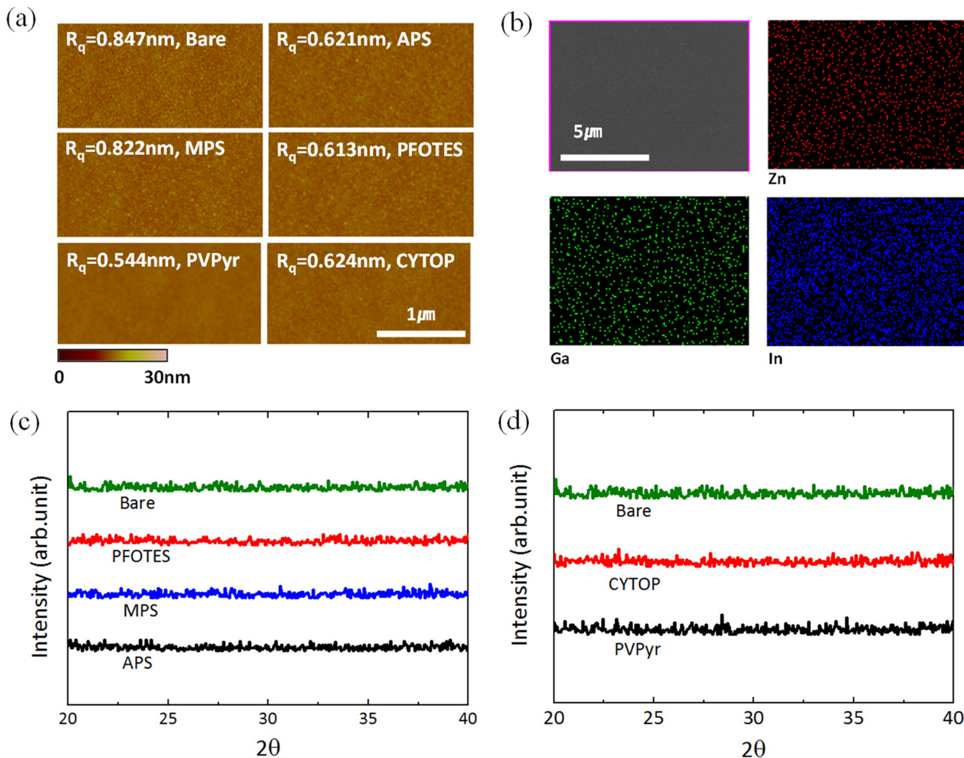

FIG. 3. (Color online) AFM topographs of the a-IGZO films on (a) bare SiO_2, APS-, MPS-, PFOTES-treated SiO_2 dielectrics, and PVPyr, CYTOP thin-films coated SiO_2. (b) A SEM image and corresponding EDS images of Zn, Ga, and In atoms of a-IGZO films deposited on PVPyr-coated SiO_2 dielectrics. XRD profiles of a-IGZO films depending on the (c) SAM and (d) polymer.

observed for organic semiconductors, such as pentacene, the grain size, and shape of which depend on the dielectric surface.[9] Therefore, the electrical performances of the a-IGZO TFTs were thought to be mainly affected by the surface dipole at the semiconductor–dielectric interface.

The influence of various dielectric surfaces on the electrical characteristics of the a-IGZO TFTs was characterized by fabricating bottom gate/top contact a-IGZO TFTs using the surface-modified gate dielectrics. Heavily doped n-type silicon wafers with 300 nm thick thermally grown SiO_2 layers were used as the gate substrates. The SAMs were prepared on the cleaned silicon wafers using a dipping method following the procedure reported in the literature. The polymer thin films were made using spin-coating methods.[15] After forming the surface modification layers, a 40 nm thick a-IGZO active layer was deposited using an RF magnetron sputtering system with an a-IGZO target composed of In_2O_3:Ga_2O_3:ZnO = 1:1:2 mol. % through a shadow mask. During deposition, the conditions, such as the RF power, working pressure, gas ratio, and substrate temperature were set to 50 W, 7 mTorr, Ar:O_2 ratio of 100:2 sccm, and 180 °C (for SAM-treated devices) or 100 °C (for polymer-coated devices), respectively.[16] To accurately compare all devices, the treated substrates were simultaneously deposited under identical sputtering conditions. One-hundred nanometer source/drain electrodes were successively deposited onto the a-IGZO films via thermal evaporation of Al through a shadow mask that defined 150 μm channel lengths (L) and 1500 μm widths (W). All electrical properties of the fabricated devices were measured using a Keithley 2400 and 236 Source Meter Instrument in ambient air. Figure 4 shows the source–drain current on a logarithmic scale as a function of the gate voltage (I_D–V_G) transfer curves in the saturation region at $V_D = 80$ V. The capacitance of all of the surface-modified gate dielectrics is almost identical to that of bare 300 nm-thick SiO_2 dielectric (i.e., 10 nF/cm^2). The transistor characteristics are summarized in Table I. The device mobilities (μ) and threshold voltages (V_{th}) were calculated in the saturation regime using the equation $I_D = (WC_i/2L)\mu(V_G\text{-}V_{th})^2$, where I_D is the drain current, V_G is the gate voltage, and C_i is the capacitance per unit area of the dielectrics.

During the sputtering of a-IGZO on top of the soft polymers, plasma damage has to be considered and need to be studied. To investigate the effect of plasma on the polymer gate dielectrics, we exposed the polymer-coated (CYTOP and PVP) SiO_2 gate dielectrics to plasma for 30 s and characterized the surface roughness and thickness of the polymer layer. The plasma condition is the same with the experimental condition for a-IGZO deposition. Because the plasma damage would gradually decrease due to the early deposited a-IGZO layer, initial dozens of seconds of plasma exposure should be critical to the polymer dielectrics. As a result, although surface roughness values slightly increased after

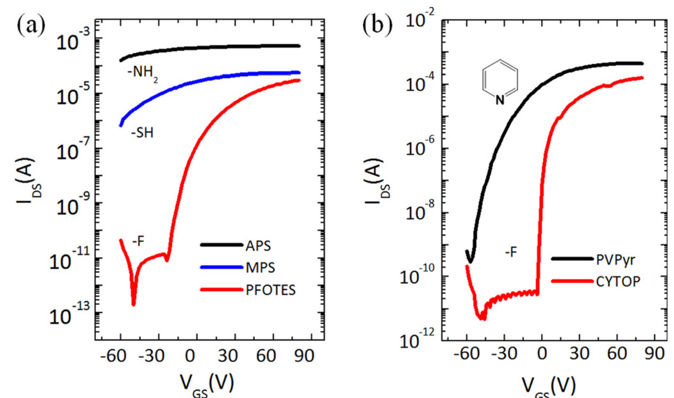

FIG. 4. (Color online) Drain current–gate voltage (I_D–V_G) transfer characteristics of a-IGZO TFTs with (a) SAM-treated and (b) thin polymer treated SiO_2 dielectrics.

TABLE I. Electrical parameters for a-IGZO TFTs prepared with SAM- and polymer-treated SiO_2 dielectrics.

		μ (cm^2/V s)	I_{on}	I_{off}	I_{on}/I_{off}	V_{th} (V)
SAM	APS	—	5.25×10^{-3}	1.54×10^{-3}	3.41	–
	MPS	1.21	5.54×10^{-4}	6.70×10^{-6}	8.26×10^{1}	−69.4
	PFOTES	1.18	3.06×10^{-4}	1.96×10^{-12}	1.56×10^{8}	2.06
Polymer	PVP	1.73	4.35×10^{-4}	2.85×10^{-10}	1.52×10^{6}	−32.3
	CYTOP	1.04	3.06×10^{-4}	1.96×10^{-12}	1.56×10^{8}	−0.55

plasma exposure, they still maintained under 0.8 nm. Moreover, thicknesses of the plasma-exposed ultra-thin polymer films were found to be almost the same with those of bare films, which indicates no severe degradation of polymer films (data not shown). Because the plasma exposure similarly affects all organic gate dielectric materials for the short moment, we speculate that the relative difference of surface dipoles for the organic material-treated gate dielectrics is still valid.

As shown in Fig. 4(a), the value of V_{th} for the devices tended to shift toward the positive direction as the SAM electron withdrawal properties increased. The a-IGZO TFTs with a PFOTES-treated SiO_2 dielectric yielded a more positive V_{th} (2.06 V) than was observed with the APS-coated SiO_2 dielectric (–69.4 V). The devices with APS-treated dielectrics even showed conductor-like behavior due to electron overflow in the channel regions. The transfer curves and electrical characteristics of the devices made with polymer-coated dielectrics showed trends similar to those shown in Fig. 4(b) and Table I; the V_{th} values increased from −32.3 V (for PVPyr samples) to −0.55 V (for CYTOP samples). These results were closely related to the surface dipole effects introduced by the SAMs and the polymer thin films at the dielectric surface. As the dielectric surface withdrew electron from the a-IGZO, a higher gate bias was needed for the device operation.[10] Our study clearly shows that the charge carrier density in the channel region, and hence the TFT performance of a-IGZO thin film, can be controlled by modifying the gate dielectric surface with organic materials.

In summary, we investigated the effects of organic dielectric surfaces on the TFT characteristics of an inorganic semiconductor, a-IGZO. By treating a SiO_2 dielectric surface with two kinds of organic materials, SAMs and polymer thin films, a-IGZO-based TFTs using various organic material-treated gate dielectrics were fabricated. The SAMs and polymer thin films with electron-withdrawing or -donating functional groups, respectively, decreased or increased the electron carrier density in the a-IGZO channel region. Accordingly, stronger surface dipoles withdrew electrons, and a more positive gate bias was required to switch on the a-IGZO TFTs, which resulted in a positive shift in V_{th}.

The XRD experiments were performed at the 10C1 beamline (wavelength ~ 1.54 Å) of the Pohang Accelerator Laboratory in Korea. This work was supported by a grant from the Strategic Technology under the Ministry of Knowledge Economy (MKE); a grant from the Korea Science and Engineering Foundation (KOSEF) funded by the Korea government (MEST) (20110000330) and also by a grant from LG Chem, Ltd.

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