

Modulating indium gallium zinc oxide transistor characteristics with discrete redox states of molecules embedded in the gate dielectric

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A hybrid inorganic-organic device has been fabricated by incorporating redox active molecules in indium gallium zinc oxide thin film transistors. These devices show a clear modulation of source-drain current characteristics, which is associated with the quantized energy states of the redox active molecules. The molecules show discrete redox peaks in the current characteristics of transistors and a true-molecular-based charge transport has been demonstrated in a completely solid state device. © 2008 American Institute of Physics. [DOI: 10.1063/1.2918981]

Molecular electronics¹⁻⁴ thrive on the synergistic coupling of molecules with devices for applications in electronics, sensing, energy harvesting, and medicine. Molecules offer several advantages for electronic applications such as nanoscopic size, discrete redox states, synthetic tailorability, low voltage of operation, and charge storage ability. Redox active molecules such as porphyrins, can store charge in multiple discrete redox states with high densities, which can be synthetically designed.⁵⁻⁷ Redox active molecules with electrolyte gates were incorporated in silicon MOSFETs (metal-oxide-semiconductor field effect transistors) and have shown clear presence of redox behavior.^{6,8} However, the low thermal budget of molecules makes them incompatible for integration with Si complementary metal-oxide semiconductor technology. In addition, the use of electrolyte gates poses a major challenge in the integration of molecular devices. Therefore, a low temperature compatible semiconductor with a solid state top contact is critical in assessing the potential of redox molecules.

Recently, low temperature compatible indium gallium zinc oxide (IGZO) has shown extremely high electron mobility (10–50 cm²/V s) in the amorphous state^{9,10} as compared to amorphous silicon (1 cm²/V s) and organic semiconductors (<1 cm²/V s).¹¹ The high mobility of IGZO semiconductors, typically fabricated at room temperature, was attributed to high degree of overlap of the spherically symmetric cationic orbitals that makeup the conduction band.^{9,10} IGZO thin film transistors (TFTs) are transparent, flexible, and can be formed at low temperatures, making them compatible with molecule incorporation. In this work, we demonstrate a hybrid inorganic-organic device where redox active molecules are incorporated in IGZO TFTs and contacted via a solid state electrode. These devices produce clear modulation of the source-drain current characteristics associated with the quantized energy states of molecules.

Figure 1(a) shows the schematic of the hybrid molecular-IGZO device. In this study, hybrid molecular IGZO TFTs were fabricated on glass substrates coated with 200 nm sputtered indium tin oxide (ITO) and a 220 nm AlO_x-TiO_x superlattice (ATO) deposited by atomic layer deposition (ALD).¹² In the transistor structures, ITO is the bottom gate electrode and ATO is the dielectric. Two differ-

ent redox molecular assemblies were studied. The first one comprises of porphyrin polymers (Por-P) molecules, to form ultrathin polymers with two redox states, which are monovalent and divalent. In the second set of molecules, porphyrins are conjugated with ferrocene (Por-Fc) (Ref. 13) to result in a system having three redox states. Molecules were dissolved in propylene glycol monomethyl ether acetate, spun on the ATO surface, and subsequently heated at 350 °C in an Argon-purged environment to form the assemblies. A thin layer of HfO₂ with varying thicknesses was formed on top of the molecules by ALD. This was followed by the deposition of a 50 nm IGZO film by using room temperature pulsed laser deposition at an oxygen partial pressure of 25 mTorr. A commercial ITO target was ablated to deposit 200 nm thick source and drain electrodes. The channel and the source/drain electrodes were patterned by using standard photolithographic and lift-off techniques. Two control samples were also included: control 1, where IGZO was directly deposited on ATO (ITO/ATO/IGZO/ITO), and control 2, where IGZO was deposited on the HfO₂/ATO surface (ITO/ATO/HfO₂/IGZO/ITO). Electrical analyses were performed by using an HP 4155B semiconductor parameter analyzer.

The cross-sectional high resolution transmission electron micrograph (HRTEM) of the device in Fig. 1(b) shows uniform and abrupt interfaces for the molecular, HfO₂, and

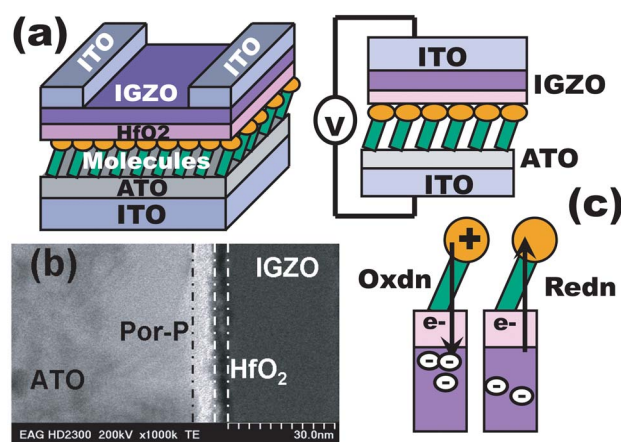


FIG. 1. (Color online) (a) Schematic of the hybrid molecular-IGZO TFT. (b) HRTEM of Por-Fc TFT (c) Schematics showing the oxidation and reduction of the redox active molecules under applied bias to exchange electrons with IGZO through HfO₂.

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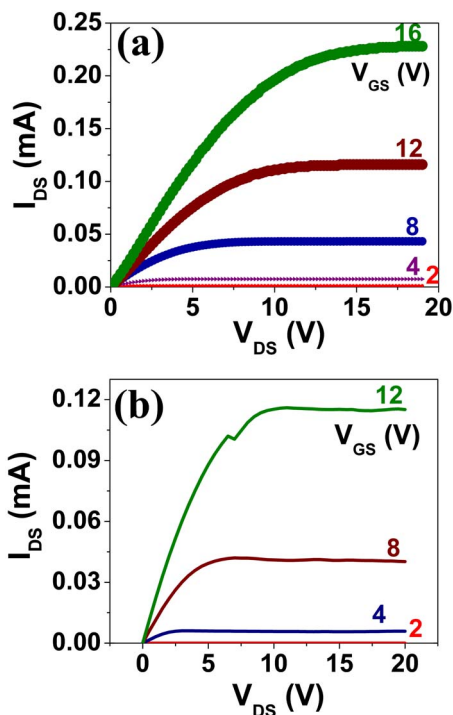


FIG. 2. (Color online) I_{DS} - V_{DS} characteristics for (a) control 1 (ITO/ATO/IGZO/ITO) and (b) Por-Fc TFT (ITO/ATO/Por-Fc/HfO₂(10 Å)/IGZO/ITO). TFT dimensions: $L=100 \mu\text{m}$ and $W=400 \mu\text{m}$.

IGZO layers. IGZO layer is amorphous as indicated by the absence of any observable grain structure. This is further substantiated by a featureless x-ray diffraction pattern for IGZO film deposited on a glass substrate (not shown). Densely packed and highly hydrophobic molecular assemblies are typically known to resist the growth of ALD layers.¹⁴ However, the molecular assemblies formed herein are believed to have a significant number of pinhole defects owing to the bulky size of porphyrins. Hence, we believe that ALD precursors can penetrate the molecular layer through pinholes to reach the molecule-ATO interface. The dielectric initially grows through the pinholes and subsequently forms a continuous layer on the molecules.¹³ A detailed discussion on the dielectric-molecular interface based on x-ray photoelectron spectroscopy and electrical measurements will be reported in a future communication.

The electrical characterization of drain current was performed on the fabricated transistors. In these transistors, redox molecules are expected to exchange electrons with IGZO through the ultrathin HfO₂ tunnel barrier [Fig. 1(c)]. When an oxidizing gate voltage is applied, molecules lose electrons to IGZO resulting in a positively charged molecular layer, which shifts the V_T to more negative values.⁸ When a reducing gate voltage is applied, molecules return to their neutral state by accepting electrons from IGZO, which brings the V_T back to its original value. Additionally, V_T shifts can occur due to the charge trapping within the organic layer. Thus, the magnitude of V_T shift (ΔV_T) depends on both the redox charges and the background traps in the molecular layer. The current versus drain voltage (I_{DS} - V_{DS}) curves for the control 1 device is shown in Fig. 2(a). Well-behaved characteristics of linear and saturation regimes are observed with a threshold voltage of 2 V. The n -type carriers in IGZO TFT control device show a mobility of $11 \text{ cm}^2/\text{V s}$. Upon the incorporation of molecules, the I_{DS} characteristics exhibit

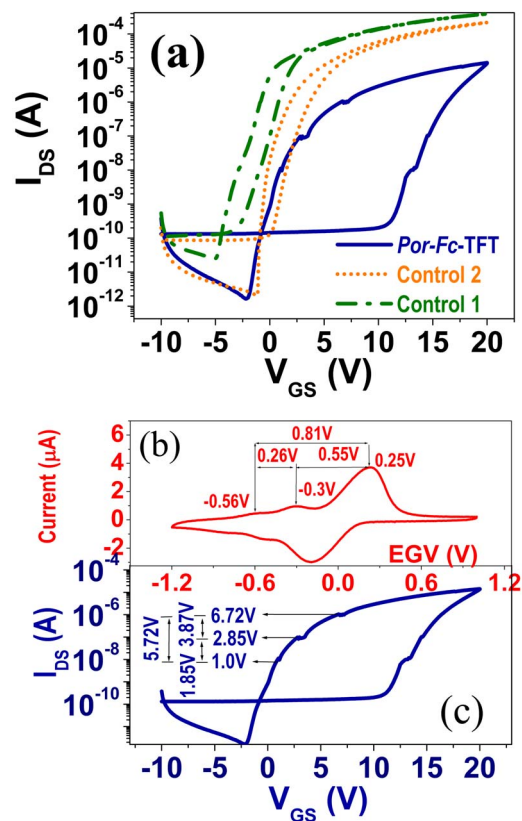


FIG. 3. (Color online) (a) $[\log(I_{DS}-V_{GS})]$ for Por-Fc TFT [ITO/ATO/Por-Fc/HfO₂(10 Å)/IGZO/ITO] (solid), control 1 (dash dot), and control 2 [ITO/ATO/HfO₂(10 Å)/IGZO/ITO] (dot). (b) Cyclic voltammogram of Por-Fc molecules measured by using electrolyte and silver wire at a scan rate of 100 V/s . The peaks in the upper half correspond to oxidation and the peaks in the lower half correspond to reduction. EGV is electrolyte gated voltage (c) I_{DS} - V_{DS} characteristics for Por-Fc TFT (ITO/ATO/Por-Fc/HfO₂(10 Å)/IGZO/ITO). The total oxidation window and the peak voltage separation between the three redox states of Por-Fc molecules have been indicated.

marked changes. As seen in Fig. 2(b), Por-Fc TFT shows the presence of peaks in the I_{DS} characteristics, which are clearly absent in the control devices. Distinct redox peaks are also seen in the I_{DS} - V_{GS} curves for Por-Fc TFT, which are again absent in both the control devices [Fig. 3(a)]. We attribute the three peaks to the three redox states of the Por-Fc molecules, i.e., monocationic and dicationic states of porphyrin and a monocationic state of ferrocene. The voltages at which these peaks occur in the above FET are larger in values compared to the traditional electrochemical voltammetric measurements wherein electrolyte were used [Figs. 3(b) and 3(c)]. In the FET structure, a dielectric surrounds the molecules and can absorb part of the applied bias. This results in a voltage divider effect that can increase both the magnitude of the oxidation potentials and the separation between the peaks. As a result, the total oxidation window of the solid state FET system increased to 5.7 V compared to 0.8 V obtained from electrochemical measurements of Por-Fc molecules [Figs. 3(b) and 3(c)]. The peak separation between the ferrocene and the first porphyrin peak occupied $\sim 66\%$ of the total oxidation window, whereas the peak separation between the first and second porphyrin peaks occupied $\sim 33\%$ of the oxidation window, which matches the distribution observed in electrochemical measurements [Fig. 3(b)]. To compare these to the expected values, we calculated the voltage separation between the three redox states when the dielectric lay-

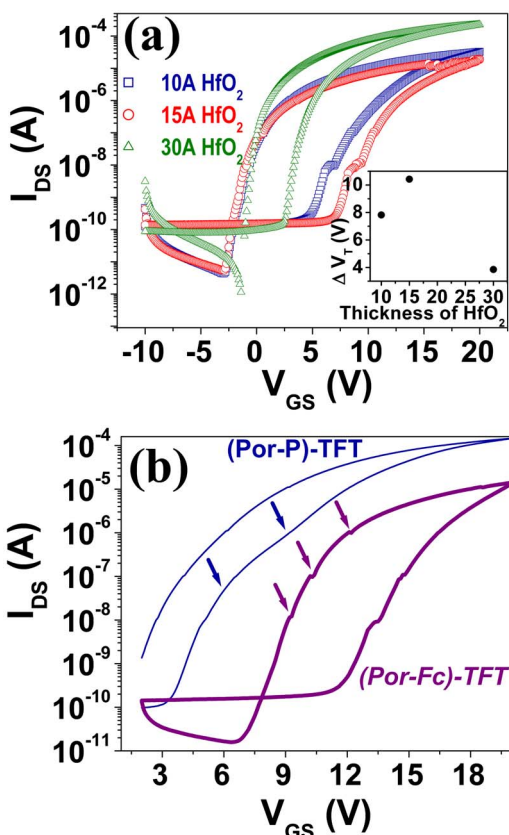


FIG. 4. (Color online) (a) I_{DS} - V_{GS} curves for Por-Fc TFTs with the variation in thickness of HfO_2 as the tunneling barrier. The inset shows the extent of V_T shift with change in the tunneling barrier. $V_{DS}=10$ V. (b) Transfer characteristics of molecular-embedded TFTs comprising Por-Fc (thick line) and Por-P (thin line) molecules with 10 Å of HfO_2 as the tunneling barrier. Redox states are indicated with arrows. $V_{DS}=10$ V.

ers of ATO and HfO_2 are placed along with the Por-Fc molecules in the stack. The permittivity and thickness $\{\epsilon, t\}$ for the ATO, HfO_2 and Por-Fc layers were taken to be $\{16, 2200\}$, $\{25, 15\}$, and $\{2, 37.5\}$, respectively. In a total oxidation window of 6.77 V, we obtain a voltage difference of 2.17 V (32%) between the ferrocenyl peak and the first porphyrin redox state, and 4.6 V (68%) between the first and second porphyrin peaks, which are in good accordance with the results obtained in the FET measurements. Hence, the observation of redox peaks at room temperature is attributed to the individual size of molecules that act as quantum dots even when they are a part of an assembly. The presence of discrete redox peaks in the drain current characteristics of a complete solid state device is a new finding in the area of molecular electronics. Although we have previously reported the modulation of capacitance in two-terminal solid state devices incorporating redox active molecules,¹³ no distinct redox peaks were observed in that structure. We believe that the use of a FET device amplifies the presence of redox charge states that can then manifest themselves as peaks in the drain current.

To further investigate the ability of redox molecules to modulate the drain current peaks, the thickness of HfO_2 layer was varied. As shown in Fig. 4(a), clear peaks are observed in I_D for both the 10 and the 15 Å HfO_2 barriers, which are

indicative of efficient tunneling. However, no peaks were observed for 30 Å of HfO_2 , which is attributed to higher tunneling barrier. The charging and discharging of the Por-Fc TFT produces a large hysteresis in the I_{DS} characteristics of Por-Fc TFT as compared to the control samples [Fig. 4(a)]. As mentioned earlier, this hysteresis can be attributed to (i) redox charges and (ii) background trapping within the molecular layer. Correspondingly, as the HfO_2 thickness is changed, the hysteresis also follows the same trend as the discrete peaks since both charging mechanisms are dependent on the tunnel barrier thickness. Finally, ultrathin Por-P with two porphyrinic redox states were also investigated. As expected, Por-P TFT shows two discrete redox states in the I_{DS} characteristics as opposed to three discrete states observed for the Por-Fc TFT [Fig. 4(b)], further confirming that the modulation of drain current characteristics occurs due to the redox states of the molecules.

We have demonstrated a complete solid state device with molecular-based charge transport by using an inorganic-organic hybrid transistor. IGZO channel materials are synergistic with molecular incorporation based on their low temperature compatibility. Molecules incorporated in IGZO TFTs have displayed discrete peaks in the source-drain characteristics, which are associated with molecular quantized states. This approach enables the assembly of nanoscale charge storage islands with a high degree of uniformity and repeatability, and offers precise single-electron transport at room temperature. Finally, the added benefits of flexibility and transparency of IGZO can lead to the emerging technological solutions of these hybrid devices, which are not achievable with silicon-based electronics.

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- ¹J. R. Heath and M. A. Ratner, *Phys. Today* **56**, 43 (2003).
- ²M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and J. M. Tour, *Science* **278**, 252 (1997).
- ³C. P. Collier, E. W. Wong, M. Belohradský, F. M. Raymo, J. F. Stoddart, P. J. Kuekes, R. S. Williams, and J. R. Heath, *Science* **285**, 391 (1999).
- ⁴Y. Q. Xue, S. Datta, and M. A. Ratner, *J. Chem. Phys.* **115**, 4292 (2001).
- ⁵Z. Liu, A. A. Yasserli, J. S. Lindsey, and D. F. Bocian, *Science* **302**, 1543 (2003).
- ⁶S. Gowda, G. Mathur, Q. Li, S. Surthi, Q. Zhao, J. S. Lindsey, D. F. Bocian, and V. Misra, *Tech. Dig. - Int. Electron Devices Meet.* **2004**, 707.
- ⁷K. M. Roth, A. A. Yasserli, Z. Liu, R. B. Dabke, V. Malinovskii, K. Schweikart, L. Yu, H. Tiznado, F. Zaera, J. S. Lindsey, W. G. Kuhr, and D. F. Bocian, *J. Am. Chem. Soc.* **125**, 505 (2003).
- ⁸S. Gowda, G. Mathur, Q. Li, S. Surthi, and V. Misra, *IEEE Trans. Nanotechnol.* **5**, 258 (2006).
- ⁹K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, and H. Hosono, *Nature (London)* **432**, 488 (2004).
- ¹⁰A. Suresh, P. Wellenius, A. Dhawan, and J. Muth, *Appl. Phys. Lett.* **90**, 123512 (2007).
- ¹¹C. D. Dimitrakopoulos and D. J. Mascarim, *IBM J. Res. Dev.* **45**, 11 (2001).
- ¹²ITO/ATO substrates supplied by Planar Systems Inc. Espoo, Finland, art_pakkala@planar.com.
- ¹³Z. Chen, B. Lee, S. Sarkar, S. Gowda, and V. Misra, *Appl. Phys. Lett.* **91**, 173111 (2007).
- ¹⁴R. Chen, H. Kim, P. C. McIntyre, and S. F. Bent, *Chem. Mater.* **17**, 536 (2005).