

Charge Storage Effect on In<sub>2</sub>O<sub>3</sub> Nanowires with Ruthenium Complex MoleculesInsung Choi<sup>1,2</sup>, Junghyun Lee<sup>1</sup>, Gunho Jo<sup>3</sup>, Kyoungja Seo<sup>1</sup>, Nak-Jin Choi<sup>4</sup>, Takhee Lee<sup>3</sup>, and Hyoyoung Lee<sup>1,2\*</sup><sup>1</sup>National Creative Research Initiative, Center for Smart Molecular Memory, Electronics and Telecommunications Research Institute, Daejeon 305-350, Korea<sup>2</sup>Next Generation Device Engineering, University of Science and Technology, Daejeon 305-333, Korea<sup>3</sup>Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, Korea<sup>4</sup>Nano Convergence Sensor Team, Electronics and Telecommunications Research Institute, Daejeon 305-350, Korea

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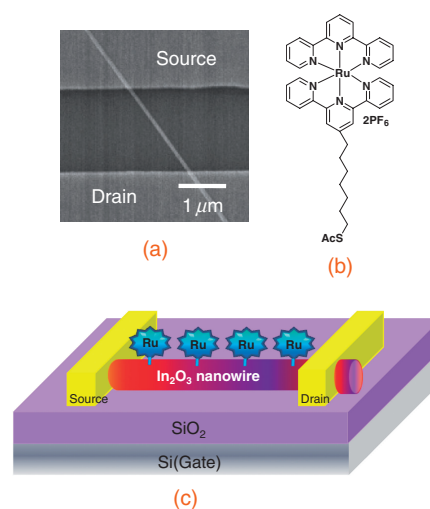
Charge storage effect on In<sub>2</sub>O<sub>3</sub> nanowire field-effect transistors (FETs) is controlled by a chemical gate, ruthenium(II) terpyridine (Ru<sup>II</sup>-tpy) complex molecules. In<sub>2</sub>O<sub>3</sub> nanowire FETs functionalized with a self-assembled monolayer of the molecules exhibit large hysteretic characteristics with regard to source–drain current vs gate voltage characteristics. The devices are operated with reversible switching behavior at gate voltage cycles of writing, reading, erasing, and reading, and their retention time is in excess of 1000 s. These results reveal that the reversible chemical reaction (i.e., oxidation and reduction of the molecules) of Ru<sup>II</sup>-tpy complexes produces a charging/discharging process of In<sub>2</sub>O<sub>3</sub> nanowire FETs. © 2009 The Japan Society of Applied Physics

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One-dimensional nanowires have attracted considerable attention because of their potential application in nanoelectronic and optoelectronic devices.<sup>1,2</sup> For example, various semiconducting nanowires such as GaN, Si, ZnO, and In<sub>2</sub>O<sub>3</sub> have been extensively studied for use in single-electron transistors, resonant tunneling diodes, memory devices, light-emitting diodes, and optical sensors.<sup>3–7</sup> Moreover, because nanowires that include an In atom are easily bound with a thiolate group, In<sub>2</sub>O<sub>3</sub> nanowires have been used for organic-semiconductor hybrid devices.<sup>8–11</sup> Redox-active molecules can act as an electrochemical gate that controls the electrical properties of nanowires, and the data storage effect of nanowire field-effect transistors (FETs) is carried out by different redox states of the molecules.<sup>8–10</sup> Despite these attractive data storage features of nanowires, the intrinsic properties of redox-active molecules in molecular memory devices with nanowires have seldom been reported.

In this study, ruthenium(II) terpyridine (Ru<sup>II</sup>-tpy) complexes with alkyl chains are used to control the charge storage effect on In<sub>2</sub>O<sub>3</sub> nanowire FETs, whose long alkyl chains can be expected to form an ordered self-assembled monolayer (SAM). The Ru<sup>II</sup>-centered complexes exhibit stability in their chemical and electrical properties during redox reactions. The voltage-driven conducting switching of an Ru<sup>II</sup>-tpy complex was revealed by means of scanning tunneling microscopy.<sup>12</sup> Thus, the Ru<sup>II</sup>-tpy complex is expected to act as a chemical gate in molecular memory based on semiconductor nanowires. We report on source–drain current vs gate voltage characteristics revealing the charge storage effect of In<sub>2</sub>O<sub>3</sub> nanowire FETs functionalized with Ru<sup>II</sup>-tpy complexes. We show that devices functionalized with Ru<sup>II</sup>-tpy complexes exhibit large hysteretic characteristics. This current hysteresis is addressed by the chemical reaction-induced band shift of an In<sub>2</sub>O<sub>3</sub> nanowire, which ensures the devices have stable, reversible switching behavior with a long retention time.

The In<sub>2</sub>O<sub>3</sub> nanowire is synthesized with a carbothermal reduction method<sup>13,14</sup> and used in a channel of FET devices fabricated in accordance with methods described in the literature.<sup>14,15</sup> After the fabrication of the In<sub>2</sub>O<sub>3</sub> nanowire FETs, a Ru<sup>II</sup>-tpy complex SAM on the surface of an In<sub>2</sub>O<sub>3</sub>

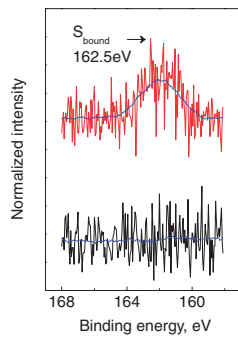


**Fig. 1.** (a) Scanning electron microscope image of an In<sub>2</sub>O<sub>3</sub> nanowire FET. (b) Molecular structure of a centered Ru<sup>II</sup> and alkanethiol-tethered terpyridine ligand complex. (c) Schematic diagram of the In<sub>2</sub>O<sub>3</sub> nanowire FET device functionalized with a SAM of alkanethiol-tethered Ru<sup>II</sup>-tpy complexes.

nanowire was formed by immersing the nanowire FETs into a molecular solution.<sup>10</sup> All the current-voltage measurements were taken in a low-vacuum chamber to avoid any influence of moisture (with pressure of approximately 10<sup>−3</sup> Torr).

Figure 1(a) shows a scanning electron microscope image of an In<sub>2</sub>O<sub>3</sub> nanowire FET: the nanowires used in this study have diameters ranging from 70 to 100 nm and channel lengths of 2–4 μm. The Ru<sup>II</sup>-tpy complexes [Fig. 1(b)] were synthesized and characterized.<sup>16</sup> The Ru<sup>II</sup>-tpy complexes were fairly stable upon exposure to air and moisture in a solution and in a solid state. The reversible electron-transfer behavior of Ru<sup>II</sup>-tpy complexes was characterized by solution-phase and solid-phase cyclic voltammograms (CVs), which show a redox reaction of Ru<sup>II</sup>/Ru<sup>III</sup>.<sup>16</sup> Figure 1(c) depicts a schematic diagram of the In<sub>2</sub>O<sub>3</sub> nanowire FET functionalized with a SAM of alkanethiol-tethered Ru<sup>II</sup>-tpy complexes. The molecular monolayer formation of the Ru<sup>II</sup>-tpy complexes was characterized by means of ultraviolet spectroscopy<sup>12</sup> and X-ray photoelectron spectroscopy (XPS). Indium tin oxide (ITO) electrodes were used as a substrate instead of In<sub>2</sub>O<sub>3</sub> nanowire.<sup>17</sup> A sulfur atom of the Ru<sup>II</sup>-tpy complex [Fig. 1(b)] can bind to an

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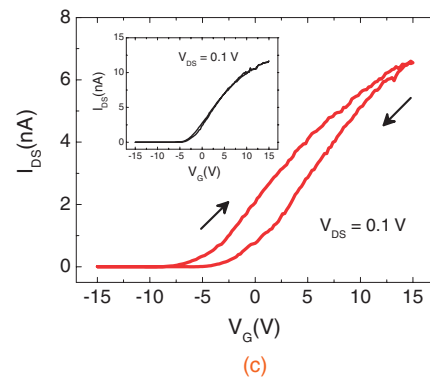
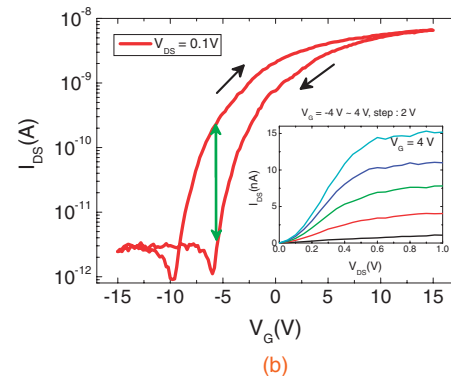
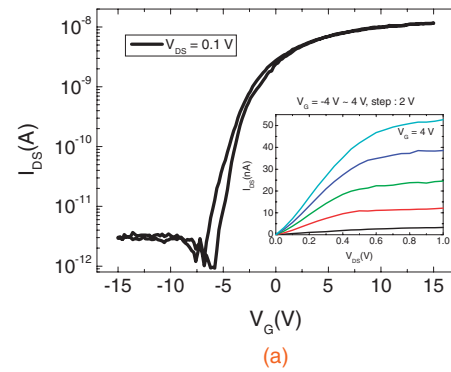


**Fig. 2.** XPS spectra for the sulfur of an ITO film with modified Ru<sup>II</sup>-tpy complexes (upper) and of a bare ITO film (lower). Raw data are smoothed with an adjacent averaging of origin program (blue lines).

indium atom,<sup>18)</sup> and XPS detects any sulfur atom of the molecules that has bound to the surface.<sup>19)</sup> Figure 2 presents the XPS spectra of a bare ITO surface (without a molecule SAM, a black line) and a functionalized ITO surface with self assembled Ru<sup>II</sup>-tpy complexes (a red line) in the range of 158 to 168 eV. The peak of 162.5 eV indicates sulfur atom's binding energy (i.e., S2p) on the surface.<sup>19)</sup> The peak-associated sulfur oxides are not evident at binding energies greater than 166 eV;<sup>19)</sup> the lack of a peak in this range in Fig. 2 indicates that there is no binding of a sulfur atom to an oxide atom. Thus, the XPS spectra confirm that alkanethiol-tethered Ru<sup>II</sup>-tpy complexes are bound well with the surface through indium-sulfur bonds.<sup>18)</sup> Furthermore, electrochemical characteristics of the Ru complex SAM on ITO have been examined by cyclic voltammetry. The CVs show that the Ru<sup>II</sup> terpyridine complex molecules on ITO can electrochemically and reversibly react to the applied voltage.<sup>12)</sup>

The inset of Fig. 3(a) shows output characteristics (source-drain current versus voltage,  $I_{DS}$ - $V_{DS}$ ) obtained from a single In<sub>2</sub>O<sub>3</sub> nanowire FET for different gate voltages ( $V_G$ ) ranging from -4 to 4 V with a 2 V step. This behavior is in agreement with the well-known fact that an In<sub>2</sub>O<sub>3</sub> nanowire is an n-type semiconductor<sup>20,21)</sup> due to the oxygen vacancies.<sup>14)</sup> Figure 3(a) shows the transfer characteristics (source-drain current versus gate voltage,  $I_{DS}$ - $V_G$ ) of the In<sub>2</sub>O<sub>3</sub> nanowire FET at a fixed  $V_{DS}$  of 0.1 V. There is no noticeable hysteresis. The on/off current ratio is as high as 10<sup>4</sup>, and the threshold voltage is approximately -6 V. The mobility of the In<sub>2</sub>O<sub>3</sub> nanowire FET is estimated as follows: the gate capacitance ( $C_G$ ) is estimated to be  $2.61 \times 10^{-16}$  F in accordance with the relation  $C_G \approx 2\pi\epsilon\epsilon_0L/\ln(2h/r)$ , where  $\epsilon$ ,  $L$ ,  $h$ , and  $r$  are the dielectric constant of SiO<sub>2</sub>, the channel length, the oxide thickness, and the radius of In<sub>2</sub>O<sub>3</sub> nanowire, respectively.<sup>22)</sup> The transconductance,  $g_m = dI/dV_G$ , at  $V_{DS} = 0.1$  V is  $2.5 \times 10^{-8}$  A/V. Thus, from the relation of  $dI/dV_G = g_m = \mu(C_G/L^2)V_{DS}$ , the electron mobility is estimated to be 86 cm<sup>2</sup>/(V s). This mobility is comparable to previously reported values of In<sub>2</sub>O<sub>3</sub> nanowire FETs.<sup>14)</sup>

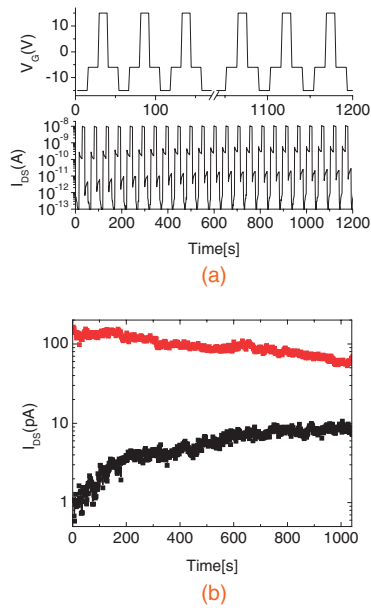
The inset of Fig. 3(b) shows n-type semiconducting behavior after the modification of the In<sub>2</sub>O<sub>3</sub> nanowire at different  $V_G$  values that vary from -4 to 4 V with a 2 V step. After functionalization with Ru<sup>II</sup>-tpy complexes, the saturation current level of the devices at  $V_G = 4$  V decreases to 15 nA (for unmodified devices). Self-assembled molecules on the Au electrode are likely to increase contact resistance. However, as the gate voltage sweeps from a negative to a



**Fig. 3.**  $I_{DS}$ - $V_G$  characteristics on a log scale of (a) an In<sub>2</sub>O<sub>3</sub> nanowire FET and (b) an In<sub>2</sub>O<sub>3</sub> nanowire FET modified with a SAM of alkanethiol-tethered Ru<sup>II</sup>-tpy complexes; the insets of (a) and (b) show  $I_{DS}$ - $V_{DS}$  characteristics of respective nanowire FETs for  $V_G$  values ranging from -4 to 4 V with a 2 V step.  $I_{DS}$ - $V_G$  characteristics on a linear scale of (c) the In<sub>2</sub>O<sub>3</sub> nanowire FET modified with a SAM of Ru complexes and [inset of (c)] the In<sub>2</sub>O<sub>3</sub> nanowire FET.

positive at a fixed value of  $V_{DS} = 0.1$  V, a threshold voltage of -9.5 V is observed [Fig. 3(b)]; and this threshold voltage is much lower than that of the unmodified device (-6 V). The threshold voltage of the In<sub>2</sub>O<sub>3</sub> nanowire FET shifts to a negative of -3.5 V after functionalization with Ru<sup>II</sup>-tpy complexes. In the reverse sweep, a large current hysteresis is observed, which indicates that the In<sub>2</sub>O<sub>3</sub> nanowire FETs modified with the Ru<sup>II</sup>-tpy complexes have an electrical bistable system. In Fig. 3(b), the double-headed arrow indicates that the position of maximum hysteresis is at  $V_G = -6$  V.

The large hysteresis of the modified In<sub>2</sub>O<sub>3</sub> nanowire FET can be explained as follows: at a large negative back-gate voltage (-9.5 V), the energy band of the In<sub>2</sub>O<sub>3</sub> nanowire is raised to deplete carriers in the In<sub>2</sub>O<sub>3</sub> nanowire, and the positive carriers can oxidize the Ru<sup>II</sup>-tpy complex molecules fixed on the In<sub>2</sub>O<sub>3</sub> nanowire. The oxidation of the molecules



**Fig. 4.** (a) Reversible switching operations in the write, read, erase, and read voltage cycles for the  $\text{In}_2\text{O}_3$  nanowire FET functionalized with alkanethiol-tethered  $\text{Ru}^{\text{II}}$ -tpy complexes: the writing, reading, and erasing voltages ( $V_G$  pulses for 1 s) are  $-15$ ,  $-6$ , and  $15$  V, respectively. (b)  $I_{\text{DS}}$  vs retention time for the  $\text{In}_2\text{O}_3$  nanowire FET in an on current state (red line) and an off current state (black line).

consequently donates electrons to the  $\text{In}_2\text{O}_3$  nanowire, resulting in an on current state of the  $\text{In}_2\text{O}_3$  nanowire FET. Conversely, a large positive gate voltage lowers the energy band of  $\text{In}_2\text{O}_3$  nanowire so that electrons accumulate on the  $\text{In}_2\text{O}_3$  nanowire, and the oxidized molecules are reduced, leading to an off current state for the  $\text{In}_2\text{O}_3$  nanowire FET. Thus, an  $\text{Ru}^{\text{II}}$ -tpy complex can work as a chemical gate to control the charge state of the  $\text{In}_2\text{O}_3$  nanowire. Figure 3(c) shows the  $I_{\text{DS}}-V_G$  characteristics on a linear scale of the  $\text{In}_2\text{O}_3$  nanowire FET modified with a SAM of Ru complexes and (inset) the  $\text{In}_2\text{O}_3$  nanowire FET.

The  $\text{In}_2\text{O}_3$  nanowire FET functionalized with  $\text{Ru}^{\text{II}}$ -tpy complexes shows a reversible switching operation in the write, read, erase, and read voltage cycles [Fig. 4(a)]. The operation cycles are implemented with writing, reading, and erasing voltage pulses of  $V_G = -15$ ,  $-6$ , and  $15$  V for 1 s,<sup>8)</sup> respectively. During the operation, the value of  $V_{\text{DS}}$  is kept at 0.1 V. No obvious degradation is evident in the current flow over 50 write–read–erase–read cycles. In addition, the retention time of the device was measured to confirm that the bistable current switching of organic-semiconductor nanowire hybrid FETs ( $\text{Ru}^{\text{II}}$ -tpy complex– $\text{In}_2\text{O}_3$  nanowire) is utilized as nonvolatile memory or programmable logic elements. Figure 4(b) shows the plots of  $I_{\text{DS}}$  vs retention time for the  $\text{In}_2\text{O}_3$  nanowire FET functionalized with  $\text{Ru}^{\text{II}}$ -tpy complexes in both the on current state (red line) and the off current state (black line). In Fig. 4(b), the initial ratio of the on current (150 pA) versus the off current (1 pA) exceeds  $10^2$ , though this value decreases slowly to a steady state. The retention time of FET devices is defined as the time taken for the on current to lose 50% to its initial value. Thus, the measured retention time of the  $\text{In}_2\text{O}_3$  nanowire FET functionalized with  $\text{Ru}^{\text{II}}$ -tpy complexes is in excess of 1,000 s. This long retention time is likely due to the existence of alkyl chains in the barrier between the active

$\text{In}_2\text{O}_3$  nanowire core and the redox-active molecule ( $\text{Ru}^{\text{II}}$ -tpy). However, the role of the alkyl chains in the operation of the devices is yet to be clearly explained. For a better understanding, further studies are needed to investigate how this barrier (for example the alkyl chains in the molecules) affects device performance, particularly in terms of charge leakage and the creation of a longer retention time.

In summary, our investigation of the electrical properties of  $\text{In}_2\text{O}_3$  nanowire devices has revealed that functionalized devices with the SAM of  $\text{Ru}^{\text{II}}$ -tpy complexes exhibit large hysteresis whereas unmodified devices exhibit no hysteresis. The variation in the nanowire channel conductance was measured in relation to the gate voltage. The write, read, erase, and read operations reveal reversible switching between the on current state and the off current state of the modified devices. The  $\text{Ru}^{\text{II}}$ -tpy complex molecule as a chemical gate via oxidation-reduction reactions can control the charge storage effect in  $\text{In}_2\text{O}_3$  nanowire devices. Our results can be helpful in the development of future nanoscale memory devices that use organic molecules based on semiconductor nanowires.

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