

## Data Storage Studies on Nanowire Transistors with Self-Assembled Porphyrin Molecules

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Detailed memory studies have been carried out based on In<sub>2</sub>O<sub>3</sub> nanowires coated with self-assembled monolayers of porphyrins. Devices with redox-active Co-chelated porphyrin coatings exhibited prominent memory effects, where the bit was represented by the charge stored in the molecules and the nanowire conductance was used as the readout. These devices exhibited reliable operation with on/off ratios of  $\sim 10^4$  and were electronically programmable and erasable. Temperature-dependent retention measurements revealed a thermal activation behavior with a barrier of 264 meV. While devices with Co-porphyrin coatings showed efficient memory operation, analogous protio porphyrin coated nanowire devices exhibited no memory effects. A largely metal-centered oxidation (e.g., Co<sup>2+/3+</sup>) appears to be important for achieving a memory effect in these devices. Our results have convincingly established a direct correlation between the molecular structure and the observed memory effect, and further in-depth studies may eventually lead to systems useful for practical applications.

Process scaling in semiconductor technology has led to a continuous increase in the density of silicon-based memories and a resulting decrease in the cost per bit. The scaling, however, will soon reach physical and technical limits, inspiring the development of new technologies for electronic memories. Molecular electronics has been proposed to circumvent the limits associated with semiconductor-based devices. Electroactive molecules can store charges through discrete redox states that are readily accessible, thus providing a viable approach for programming through oxidation and reduction reactions. Molecular memory could in principle function at nanoscale with a few electrons, and therefore promises low power and ultradense systems. There have been recent reports of molecular memory devices, constructed with molecular monolayers sandwiched between metallic contacts.<sup>1–3</sup> This approach has shown interesting device properties; however, the deposition of metals onto a monolayer of molecular wires can lead to low device yield and this problem remains a major challenge.

An alternative approach to the use of monolayers of molecular materials between metal electrodes is to utilize redox-active molecules to chemically gate charge sensitive nanostructures, such as nanotubes or nanowires. In this way it is possible to make reliable contacts to the nanotube or nanowire and control its properties with the molecular material, without having to make direct contacts to the molecules themselves. This concept was first demonstrated with nanowires coated with spun-on cobalt phthalocyanine films, which displayed intriguing memory effects.<sup>4</sup> These spun-on films, however, may lead to molecules deposited in various orientations, ranging from standing normal to lying flat on the nanowire surface. To prepare a more robust nanowire/molecular interface with better control, we prepared

dithioacetate-terminated porphyrin molecules and studied the gating effect of the self-assembled monolayers (SAM) on In<sub>2</sub>O<sub>3</sub> nanowire field effect transistors (FETs). Studies reveal that the memory effect was only observed for samples with Co-metalated porphyrins, and no memory effect was obtained with protio porphyrins. The data storage for devices with Co porphyrin was carried out by altering the redox states of the molecules, and the In<sub>2</sub>O<sub>3</sub> nanowire conductance was used as the readout. Our devices exhibited reliable operation and on/off ratios of  $\sim 10^4$ . Furthermore, we have carried out temperature-dependent memory studies for the first time with such devices, and the retention time was observed to increase as temperature decreased following an activation behavior.

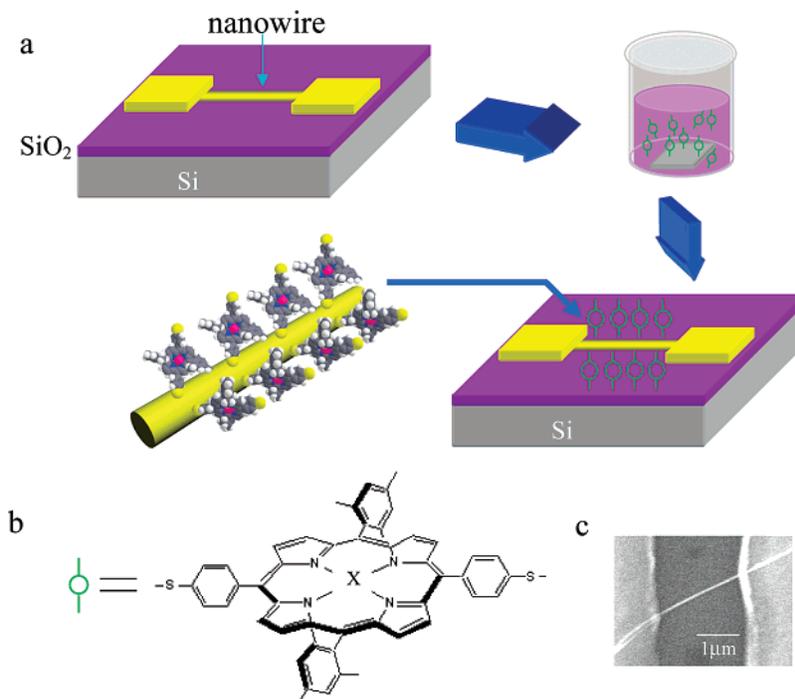
We have used a variety of nanowires for our study; here we will focus on the results from In<sub>2</sub>O<sub>3</sub> nanowires. The In<sub>2</sub>O<sub>3</sub> nanowire synthesis was performed using a laser ablation setup following the well-known vapor–liquid–solid approach.<sup>5</sup> Precise control over the nanowire diameter has been achieved by using monodispersed 10 nm gold clusters as the catalyst. These nanowires were then deposited onto a silicon wafer coated with SiO<sub>2</sub>. Source/drain electrodes, contacting the nanowires, were patterned using photolithography (shown in Figure 1a), and the silicon substrate was used as the gate electrode. Details of the growth and device fabrication can be found elsewhere.<sup>5,6</sup> These devices exhibited typical n-type field effect transistor behavior and showed no hysteresis in electrical properties when measured in vacuum. The porphyrins used here as molecular gates are illustrated schematically in Figure 1b. The nonmetalated (protio) porphyrin has X = H<sub>2</sub> in Figure 1b, while cobalt-metalated porphyrins have X = Co. Functionalization of the nanowire surface was carried out by immersing the as-fabricated devices into a 0.1–0.5 mM solution of the desired porphyrin. A small amount of aqueous NH<sub>4</sub>OH was added to the solution to convert the thioacetate groups into free thiols, which spontaneously adsorbed onto the In<sub>2</sub>O<sub>3</sub> surface and formed self-assembled

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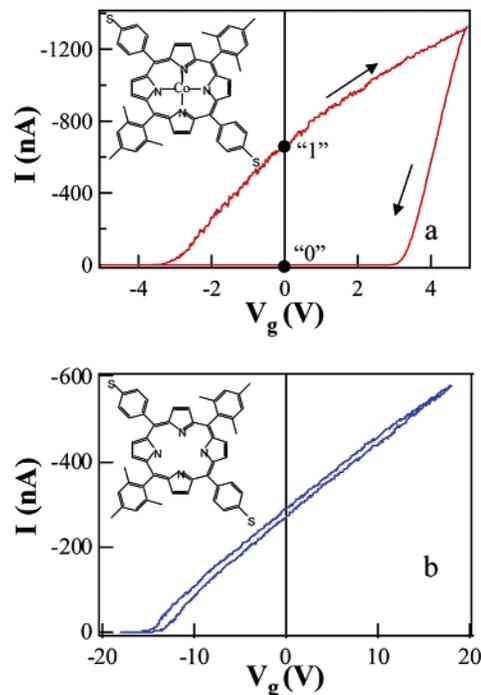


**Figure 1.** (a) Fabrication process of the memory device. An as-fabricated In<sub>2</sub>O<sub>3</sub> nanowire transistor was first immersed in a solution of the desired molecules, and self-assembly was employed to coat the In<sub>2</sub>O<sub>3</sub> nanowire with a monolayer of various porphyrin molecules. The sample was then taken out of the solution and ready for memory characterization. (b) Molecule structure of the porphyrins used in this study. (c) SEM image of an In<sub>2</sub>O<sub>3</sub> nanowire device used in this study.

monolayers,<sup>7</sup> as shown in Figure 1a. Ellipsometry was performed over test In<sub>2</sub>O<sub>3</sub> film samples to confirm the formation of monolayers. A scanning electron microscopy image of our memory devices is shown in Figure 1c.

Our memory studies were based on devices consisting of individual nanowires. The writing operation of our devices was performed by applying a negative voltage pulse to the Si back gate, which led to positive charges injected into the self-assembled molecules, leaving them in the oxidized state. The readout of the memory was performed by measuring the conductance of the In<sub>2</sub>O<sub>3</sub> nanowire with the gate bias fixed at 0 V, where the oxidized molecules should work as a chemical gate and lead to a high-conductance state for the n-type semiconductive In<sub>2</sub>O<sub>3</sub> nanowire. Vice versa, applying a positive bias to the gate can return the porphyrin to its reduced form and bring the nanowire device to a low-conductance state. The retention time of our memory devices is therefore determined by the charge retention of the redox states of the self-assembled molecular coating, which can be controlled by rational engineering of the molecular structures.

Figure 2a shows typical memory operations of an In<sub>2</sub>O<sub>3</sub> nanowire field effect transistor functionalized with a self-assembled monolayer of Co-porphyrin molecules. All measurements were carried out at room temperature with the devices residing in a high-vacuum chamber to eliminate the effect of moisture (pressure  $\sim 10^{-6}$  Torr). Our devices exhibited n-type transistor behavior both before and after the molecule deposition, as a negatively increasing gate bias can progressively reduce the nanowire conduction. However, a striking hysteresis was observed in the current (*I*) versus gate bias (*V<sub>g</sub>*) curve, as shown in Figure 2a. The source-drain bias was held constant at  $-0.1$  V, while the gate bias was swept from  $-5$  to  $5$  V. A current onset was observed for  $V_g = -3$  V; however, when  $V_g$  was swept back from  $5$  to  $-5$  V, the current decreased monotonically and reached zero around  $3$  V. Similar experiments were also performed with devices containing protio porphyrin



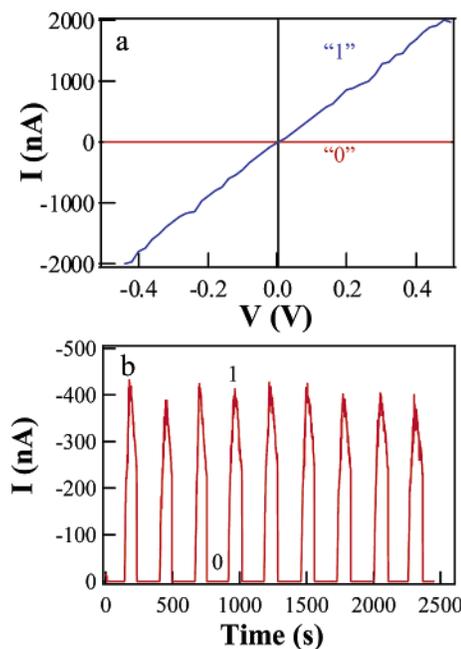
**Figure 2.** *I*–*V<sub>g</sub>* characteristics of In<sub>2</sub>O<sub>3</sub> nanowire devices with self-assembled Co-porphyrin (a) and protio porphyrin (b), respectively. Insets: structures of the corresponding molecules.

molecules using the same method, and typical *I*–*V<sub>g</sub>* curves are plotted in Figure 2b. In contrast to the large hysteresis observed with the device containing Co-porphyrin molecules, almost no hysteresis was observed for the devices functionalized with protio porphyrin. More than six devices were measured for each porphyrin, and consistent behavior was clearly observed. Our work directly links the observed memory effects to the redox states of the metal ion in the porphyrin coating. Cobalt porphyrins show facile oxidation, due to the readily accessible

Co<sup>2+/3+</sup> couple. Protio porphyrins also show oxidation states, associated with oxidation of the porphyrin  $\pi$ -system, but at higher potential than the Co-metalated analogue.<sup>8,9</sup> Thus oxidation of the Co porphyrin leads to a largely metal-centered positive charge, while the protio porphyrin has the charge delocalized over the entire porphyrin. Our results indicate that sweeping the gate bias converts the Co-porphyrin molecules to different redox states, which subsequently led to the prominent hysteresis observed in the  $I$ - $V_g$  sweep in Figure 2a. The positive charge, written to the Co porphyrins, leads to a lasting change in the nanowire conductance, whereas cycling to a high enough positive bias can erase the written information and reduce the Co porphyrin. The protio porphyrin molecules, however, do not show evidence of any lasting reduced or oxidized porphyrin states on sweeping the gate bias up to tens of volts, thus clearly illustrating the importance of the molecular porphyrin coating. Our working hypothesis is that trapping the charge on the metal center of the porphyrin (as in the Co case) leads to a largely trapped positive charge, relative to the case in the protio porphyrins, where the positive charge extends to edges of the porphyrin molecule and is thus readily transferred back to the nanowire on reverse cycling of the potential.

From Figure 2a, two memory states, one denoted state "1" and the other denoted state "0", can therefore be defined at  $V_g = 0$ . From the  $I$ - $V_g$  curve in Figure 2a, we calculated a transconductance of  $g_m = dI/dV_g = 1.56 \times 10^{-7}$  S at a source-drain bias of  $V = -0.1$  V for the sweep from  $-5$  to  $5$  V, and  $g_m = 8.30 \times 10^{-7}$  S for the sweep from  $5$  to  $-5$  V. Normalized by the width of the nanowire  $d = 10$  nm, transconductance values of 15.6 S/m and 83 S/m were thus obtained. The electron mobility can be further deduced from the transconductance of the FET.<sup>10,11</sup> In the linear regime, it is given by  $dI/dV_g = \mu(C/L^2)V$  where  $C$  is the capacitance and  $L$  is the length of nanowire. The capacitance of the nanowire is given by  $C \approx 2\pi\epsilon\epsilon_0L/\ln(2h/r) = 1.17 \times 10^{-16}$  F, where  $\epsilon = 3.9$  is the dielectric constant,  $h = 100$  nm is the thickness of the silicon oxide layer, and  $r = 5$  nm and  $L = 2$   $\mu$ m are the radius and length of the In<sub>2</sub>O<sub>3</sub> nanowire, respectively. The electron mobility was thus estimated to be 533 cm<sup>2</sup>/Vs and 2838 cm<sup>2</sup>/Vs from the transconductance values we obtained for the different gate bias sweep directions. We caution that nanowires functionalized with redox-active molecules cannot be treated as a simple field effect transistor and the above mobility values can only be used as guidance. Nevertheless, these numbers are in the high range compared to conventional semiconductors and indicate the high quality of our In<sub>2</sub>O<sub>3</sub> nanowires. From the change of the threshold voltage ( $V_t$ ) when the gate bias was swept back and forth, we can further estimate the electron concentration variation using the equation  $\Delta n = C\Delta V_t/eL = 3$  nm<sup>-1</sup>, where  $\Delta V_t = 6.8$  V is the shift of the threshold gate voltage. This estimation confirms that our memory devices operate with few electrons (3 e<sup>-</sup> per nanometer length of the nanowire).

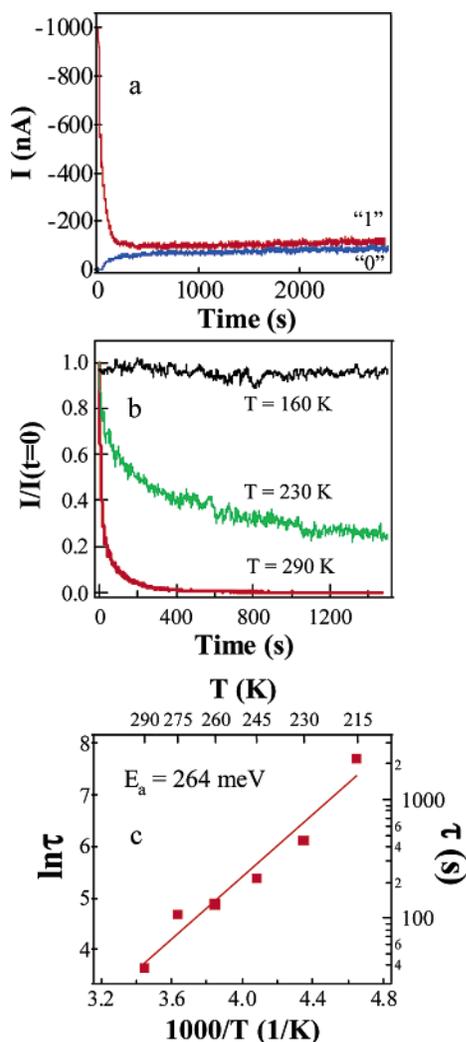
Below we focus on the operation of memory devices utilizing Co-porphyrin molecules. Writing operation was achieved by applying positive or negative voltage pulses to the gate electrode, and the memory state was read by measuring the conductance of the device with the gate electrode grounded. Figure 3a displays two  $I$ - $V$  curves, with state "1" taken after applying a  $-5$  V gate pulse and state "0" taken after a 5 V gate pulse. Careful examination revealed a conductance of  $4.28 \times 10^{-6}$  S for state "1" and  $1.16 \times 10^{-10}$  S for state "0", thus indicating an on/off ratio as high as  $3.7 \times 10^4$ . We have further tested the reliability of our memory devices, where the device was repeatedly written into state "0" and state "1" with a fixed



**Figure 3.** (a)  $I$ - $V$  curves for state "1" and state "0" of the In<sub>2</sub>O<sub>3</sub> nanowire memory with Co-porphyrin molecules. (b) Current recorded after the device was repeatedly written into states "1" and "0". Here,  $V = -0.1$  V.

source-drain bias of  $-0.1$  V. The readout after each writing operation is plotted in Figure 3b. This device showed two distinctive states, and no obvious degradation was observed after repeated writing and reading. Such reliable operation is a direct result of the present device configuration: compared to previous molecular memories using metal/molecular monolayer/metal sandwich structures,<sup>1-3</sup> the molecular materials in our devices are moved out of the conduction path, thus eliminating the most difficult reliability issues such as voltage stress, heat dissipation, and metal filament formation. Figure 3b also reveals a decrease of the current value for state "1" after each writing was performed. In contrast, the current for state "0" remained almost zero during the time duration measured, indicating that this is the default state. This is consistent with the fact that the as-synthesized Co-porphyrin has Co<sup>2+</sup> ions (reduced state) as the default state. These unoptimized devices exhibited rather slow operation ( $< 1$  kHz). This is likely limited by the high device resistance ( $0.25$  M $\Omega$  for state "1" in Figure 3a) and also high parasitic capacitance ( $C \sim 690$  pF) between the bonding pads (each  $\sim 1$  mm<sup>2</sup>) and the silicon back gate. This yields a time constant of 0.172 ms and an upper limit of 5.8 kHz for the operation frequency. We stress that future effort should be able to bring the operation frequency up to gigahertz by eliminating the parasitic capacitance and increasing the device conduction.

Bit retention as a function of time and temperature are shown in Figure 4. Current versus time curves (shown in Figure 4a) were taken at room temperature with a fixed source-drain bias  $V = -0.2$  V for both state "1" (upper curve) and state "0" (lower curve) right after the writing ( $V_g = -5$  and  $+5$  V) was performed. A relatively large decrease in the current value for state "1" was observed, whereas state "0" only exhibited a relatively small increase in current. This is consistent with the data shown in Figure 3, and once again indicates that Co<sup>2+</sup> is the more stable state for the Co-chelated porphyrin in our device structure. The retention curve for state "1" can be fitted with an expression  $Ae^{t/\tau}$ , and a retention time constant of 41 s was obtained. This device was then cooled with the bit retention measured at various temperatures. Three typical curves are



**Figure 4.** Retention measurements as a function of time and temperature. (a) Current vs time ( $I-t$ ) for states "1" and "0" measured with  $V = -0.2$  V. An exponential fit yielded a time constant of 41 s for state "1". (b) Current (normalized by  $I(t = 0)$ ) recorded for state "1" at three temperatures: 160, 230, and 290 K. (c) Temperature dependence of the retention time, indicating an activation energy  $E_a = 264$  meV.

shown in Figure 4b, corresponding to temperatures of 160, 230, and 290 K, where the y-axis represents the current normalized by the starting value  $I(t = 0)$ . One can clearly see that the retention time increased as the temperature decreased. For temperatures lower than 200 K, the device can retain the stored information for several hours without any degradation, as

illustrated by the top curve in Figure 4b. Measurements of the retention time at different temperatures yielded an exponential dependence with  $1000/T$ , as shown in Figure 4c. This indicates a thermal activation behavior as  $\tau = \tau_0 \exp(E_a/(kT))$ . The activation energy  $E_a$  for this molecule over this bias regime was found to be approximately 264 meV. More work is needed to fully elucidate the origin of this activation barrier; however, we envision that much longer retention time can be obtained with increased activation barrier height, for instance, by replacing the phenyl group in Figure 2b with alkyl groups of equal or longer length.

In summary, we have demonstrated nanoscale memory devices based on nanowire field effect transistors with self-assembled redox-active molecules. This technique creates a seamless integration of nanowires and molecular wires and yields devices with on/off ratios exceeding  $10^4$ . We have further demonstrated that metal ions in the porphyrin molecules play a key role for the observed memory effects, as only Co-chelated porphyrin yields pronounced hysteresis in the  $I-V_g$  sweeps. We believe this demonstration will be very beneficial for future nanoscale memory studies. For instance, one can envision that truly molecular scale memories can be made by scaling down the nanowire channel length to nanometers or by using quantum dots functionalized with redox-active molecules.

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