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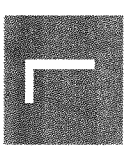
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8. Here  $r_s$  is the inter-particle distance in units of Bohr radius.
9. M. Di Ventra, S. T. Pantelides, and N. D. Lang, Phys. Rev. Lett., **84**, 979 (2000).
10. J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, and H. v. Lohneysen, Phys. Rev. Lett., **88**, 176804 (2002).
11. J. G. Kushmerick, D. B. Holt, J. C. Yang, J. Naciri, M. H. Moore, and R. Shashidhar, Phys. Rev. Lett., **89**, 086802 (2002).

### Nonvolatile Carbon Nanotube Memory Device With Molecular Charge Storage

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#### ABSTRACT

Nanoscale, non-volatile, multi-bit memory devices have been fabricated consisting of carbon nanotube field-effect transistors (CNT-FETs) surrounded by redox active molecules (cobalt porphyrin). Charge was stored in the cobalt center atom of the molecule. Write and erase programming was carried out with back-gate pulses. By varying the back-gate amplitude multi-level memory operation was achieved. Programmed devices were read at zero gate voltage showing distinct logic ON and OFF states at room temperature for several hours. At low temperatures strong increase in retention time was observed and single-electron sensitivity was demonstrated. Charge stability tests show insignificant device change after  $10^5$  write and erase cycles.

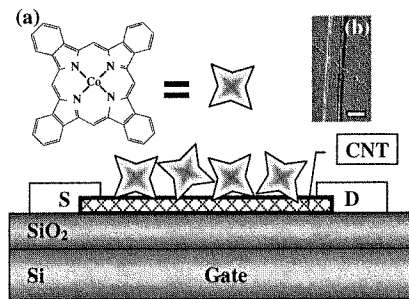
#### INTRODUCTION

With Moore's Law approaching the point where miniaturization of established "top-down" fabricated devices reaches fundamental limit within the next one or two decades, researchers are avidly pursuing alternatives to fulfill the demand for increasing computing power and information storage. "Bottom-up" approaches to Nanoelectronics can potentially reach far beyond the limits of "top-down" manufacturing. Nanoscale memory devices based on one-dimensional channels using charge traps in the underlying Si substrate oxygen-related defect trap sites near the carbon nanotubes (CNTs) or traps at the Si/SiO<sub>2</sub> interface for charge storage have been demonstrated.<sup>1,2,3</sup> These devices lack the ability to engineer the charge storage mechanism reliably. Memory devices demonstrated in this paper are based on carbon nanotube field effect transistors (CNT-FETs)<sup>4</sup> and use thin layers of redox active metal-complex molecules, cobalt porphyrin (CoP), for charge storage acting as a floating gate with naturally occurring tunnel barriers. Writing and erasing of the memory devices were carried out by applying voltage pulses to the back-gate reducing or oxidizing the CoP molecules. Due to the high mobility of a CNT-FET,<sup>5</sup> the conductance is sensitive to the stored charge in the vicinity of the active channel and hysteresis was observed when the gate was swept back and forth.

#### EXPERIMENT

CNT-FETs were fabricated using highly doped Si wafers with 110 nm thermally grown SiO<sub>2</sub>. Prior to nanotube growth, wafers were annealed under H<sub>2</sub> flow (1 l/s) at 700°C for 1 hour to reduce the trap density at the Si/SiO<sub>2</sub> interface.<sup>2</sup> Nanotubes were grown using a chemical-

vapor-deposition (CVD) method pioneered by Kong et al.,<sup>6</sup> where methane ( $\text{CH}_4$ ) gas was used as feedstock yielding high quality single-walled carbon nanotubes (SWNTs). Additional hydrogen ( $\text{H}_2$ ) gas was flown while ramping the furnace up to growth temperature ( $900^\circ\text{C}$ ) and during the cooling down.<sup>2</sup> Nanotubes were detected using atomic force microscopy (AFM) and electrically connected with the electron-beam lithography (EBL) techniques. 40 nm palladium (Pd) was electron-beam evaporated (40 nm) followed by final lift-off. Pd-contacted nanotubes have been shown to exhibit ohmic contacts with small to no Schottky barriers to semiconducting CNTs leading to high *on*-current ( $I_{\text{on}}$ ).<sup>7</sup> Figure 1(b) shows an AFM image of the device, with a channel length  $L$  of 500 nm and a diameter of  $\sim 1$  nm. CoP molecules were placed onto the chip from a 0.25 mM solution which was allowed to dry in ambient air. The solution consists of pure CoP molecules in dichloromethane without any counter anions. Figure 1(a) shows the device schematic. Completed devices were stored in nitrogen environment until they were characterized with a Keithley-4200 semiconductor analyzer in the  $\text{N}_2$  atmosphere. More than eight devices were characterized showing consistent behaviors described below.



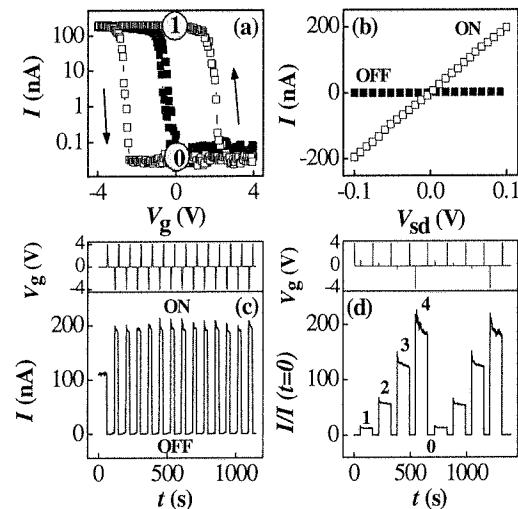
**Figure 1.** (a) Structure of a CoP molecule and schematic of a back-gated CNT-FET coated with CoP molecules fabricated on thermally-grown  $\text{SiO}_2$ . (b) AFM image of a device. Scale bar 500 nm.

## RESULTS AND DISCUSSIONS

Devices without molecule deposition or with redox-inactive metal-free porphyrin molecules showed little hysteresis in the transconductance plot when the gate was swept back and forth (Figure 2(a) filled squares). After the CoP molecule deposition a clear hysteresis was observed even in vacuum ( $10^{-5}$  torr) (Figure 2(a) open squares). At negative gate voltage where the CNT-FET is in the high conductance state (p-type), the redox molecules were oxidized ( $\text{Co}^{3+}$ -state). Thus, the positively charged molecules effectively act as a compensating chemical top gate facilitating CNT-FET depletion on the forward sweep. The converse is true for positive gate voltages leaving the molecules in the reduced  $\text{Co}^{2+}$ -state enabling the CNT-FET to be turned ON at more positive gate voltages.<sup>8,9</sup> The occurrence of hysteresis in the transconductance plot using a back gate has been previously attributed to charge traps in bulk  $\text{SiO}_2$ ,<sup>1</sup> oxygen-related defect traps in the vicinity of the CNT channel,<sup>2</sup> traps at the  $\text{Si}/\text{SiO}_2$  interface<sup>3</sup> and chemical environments, such as water.<sup>11</sup> In our case, caution was taken in the fabrication processes in order to rule out hysteresis due to effects other than charge storage in the deposited molecules in

the present devices. Annealing in hydrogen at high temperatures, sample dehydration and storage in nitrogen ensured negligible hysteresis prior to molecule deposition (Figure 2(a) filled squares).

Given the large hysteresis, we can define two memory states ON and OFF. Figure 2(a) shows these two states represented as '1' and '0' states respectively. When the gate was pulsed with  $V_p = +4$  V and  $-4$  V (to write and to erase the memory) for 2 s followed by  $I$ - $V_{\text{sd}}$  read-out, the device showed two distinct conductance states with a conductance ratio of  $9.7 \times 10^3$  (Figure 2(b)). In contrast to silicon flash memory technology where hot-electron injection employing high driving source-drain field ( $\sim 10$  V/ $\mu\text{m}$ ) is used,<sup>10</sup> here the write and erase gate pulses were applied without a simultaneous source-drain voltage. Low driving fields needed to program/erase the memory can be understood as result of two aspects: a thin tunnel barrier and high mobilities of CNTs. During memory operation electrons are exchanged between the CNT and the CoP molecules. The tunnel oxide in conventional flash memories is on the order of several nanometers. In contrast, the tunnel barrier thickness in our devices is roughly half the diameter of a CoP molecule,  $d_{\text{CoP}}/2 = 0.3$  nm. We believe that the low driving fields for our devices offer a distinct advantage for low power flash-memory technology.

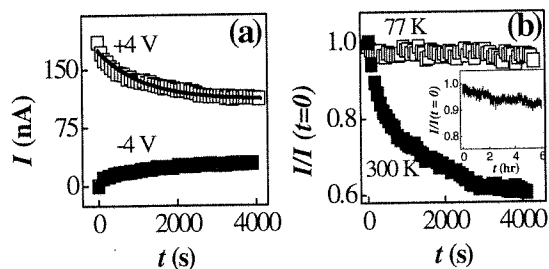


**Figure 2.** (a)  $I$ - $V_g$  for a CNT-FET device at room temperature before (filled squares) and after (open squares) CoP deposition ( $V_{\text{sd}} = 0.1$  V, sweep rate =  $0.25$  V/s). ON and OFF states denoted as 1 and 0 respectively are defined at  $V_g = 0$  V. (b)  $I$ - $V_{\text{sd}}$  characteristics recorded after device programming with  $+4$  V and  $-4$  V gate pulses for 2 s ( $V_{\text{sd}} = 0$  V). Two logic ON and OFF states were obtained with an *on-off* conductance ratio of  $\sim 10^4$ . (c) Reversible *on/off* switching of the device at  $V_{\text{sd}} = 0.1$  V using  $+4$  V and  $-4$  V gate pulses for 2 s. The gate voltage sequence is shown in the upper panel. Device shows stable characteristics after many write, erase and read operations. (d) Multi-bit programming with gate pulses of  $+1$  V,  $+0.5$  V,  $-0.5$  V and  $-4$  V. 4 different stable ON states are obtained, denoted by 1 to 4.

Reversible ON and OFF switching of was studied using gate pulses for 2 s (Figure 2(c)). A multi-bit memory cell was achieved by applying gate pulses of different amplitudes as shown in Figure 2(d). A positive gate of +4 V always turns the device fully OFF ('0' state). To test the device's endurance,  $10^5$  write and erase cycles were carried out showing only a small increase in hysteresis of  $\sim 3\%$  (not shown), which can be attributed to charge build-up in the gate oxide layer during the cycling experiment over time.<sup>16</sup>

Figure 3(a) shows retention time measurements at room temperature. Data were fitted to an exponential decay expression,  $A \cdot \text{Exp}(-t/\tau)$ , where  $\tau$  is the retention time constant (RTC) for the ON state. For this device we found  $\tau$  to be 1155 s. Compared to memory devices based on  $\text{In}_2\text{O}_3$  nanowires utilizing self-assembled monolayers of CoP molecules<sup>9</sup>, our RTC was found to exceed by a factor of 26. This can be understood as an increased tunnel barrier thickness from randomly deposited from functionalized molecules. Lieber *et al.* reported on memory devices consisting of semiconducting InP nanowires surrounded by a tunnel oxide functionalized with phthalocyanine molecules.<sup>8</sup> Our devices show comparable RTCs without the need of an oxide layer between the channel and the redox molecules, resulting in lower program/erase voltages in our devices. We believe that the charge retention time in our devices can be improved by using molecules with longer ligands.<sup>9</sup>

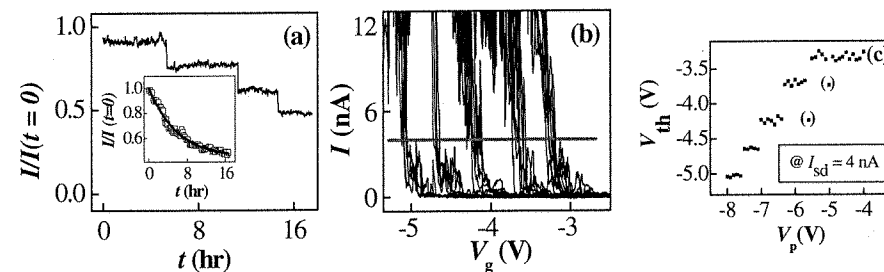
Cooling the device to 77 K led to a clear RTC increase, i.e.,  $\tau = 8.1$  hours (inset Figure 3(b)). Similar behavior of temperature-dependent tunnel barrier has been observed earlier in memory devices using  $\text{In}_2\text{O}_3$  nanowires with functionalized CoP molecules.<sup>8</sup>



**Figure 3.** (a) RTC measurement at room temperature after programming using +4 V (open squares) and -4 V (filled squares) gate pulses for 2 s,  $\tau = 1155$  s. (b) RTC comparison between room temperature (filled squares) and 77 K (open squares). Inset shows  $I/I(t=0)$  at 77 K with almost no decay over a period of 6 hours.

At the temperature of 4.2 K step-like current drops in the retention time measurement were observed (Figure 4(a)) for  $V_p = +4$  V for 10 s,  $V_{sd} = 0.1$  V. These discrete events were previously attributed to single-electron discharging effects in a CNT based memory using nanocrystals for charge storage at low temperatures<sup>2,12,13</sup>. After charging the molecules with  $V_p$ , the current through an ultra-narrow, one-dimensional channel like a CNT is modulated by the maximum potential barrier created by charged molecules along the channel.<sup>14,15</sup> Every discharge event hands the control of the current through the channel over to the next critical potential barrier, created by another charged molecule on the CNT. Single-electron discharging events are stochastically distributed and can be described by a superposition of several exponential

emission distributions with different time constants.<sup>14</sup> Averaging 10 current vs. time curves show a 'smooth', exponential decay (inset to Figure 4(a)). Single-electron events were also observed when  $V_p$  was lowered in 100 mV increments from -4 V to -8 V and  $I-V_g$  was recorded subsequently (Figure 4(b)). Clear aggregation of the threshold voltages (defined at  $I_{sd} = 4$  nA, red line) was observed). Similar single-charge conductance modulation has been reported in CNT devices<sup>12</sup> and in ultrasmall Si channels.<sup>14</sup> The effect of discrete charging/discharging events can alternatively be illustrated by plotting  $V_{th}$  as a function of  $V_p$  at a fixed  $I_{sd}$  showing the expected staircase behavior (Figure 4(c)).



**Figure 4.** (a) Retention time measurement at 4.2 K after  $V_p = 4$  V for 10 s. Discrete steps correspond to single discharge events. Inset shows 10 averaged RTC measurements and an exponential decay fit. (b) Threshold voltage evaluation for programming voltages from -4 V to -8 V in 0.1 V increments. (c) Extraction of  $V_{th}$  vs.  $V_p$  from measurements in (b) showing discrete levels in  $V_{th}$  and  $V_p$  due to single electron sensitivity of the device.

## CONCLUSIONS

In conclusion, non-volatile multi-bit nanoscale memory devices consisting of CNT-FETs coated with redox-active molecules have been assembled. Device programming with write and erase gate pulses show distinguishable ON and OFF states up to several hours at room temperature with *on/off* ratios close to  $10^4$  with retention times constants of 30 min. At low temperatures, a strong increase in the retention time was observed and single electron sensitivity was demonstrated. Endurance tests reveal stable device characteristics upon at least  $10^5$  write and erase cycles.

Compared to conventional flash memories and molecular memories demonstrated using nanowires as active channels, our devices operate with smaller program/erase voltages and is sensitive down to single electron changes, which is advantageous for low power consumption applications.

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## REFERENCES

1. M. S. Fuhrer, B. M. Kim, T. Durkop and T. Brintlinger, *Nano Lett.* **2**, 755 (2002).
2. M. Radosavljevic, M. Freitag, K. V. Thadani and A. T. Johnson, *Nano Lett.* **2**, 761 (2002).
3. J. B. Cui, R. Sordan, M. Burghard and K. Kern, *Appl. Phys. Lett.* **81**, 3260 (2002).
4. S. J. Tans, R. M. Verschueren and C. Dekker, *Nature* **393**, 49 (1998); R. Martel, T. Schmidt, H. R. Shea, T. Hertel and Ph. Avouris, *Appl. Phys. Lett.* **73**, 2447 (1998).
5. T. Durkop, S. Getty, E. Cobas and M. S. Fuhrer, *Nano Lett.* **4**, 35 (2004).
6. J. Kong, H. Soh, A. Cassell, C. F. Quate and H. Dai, *Nature* **395**, 878 (1998).
7. A. Jayey, J. Guo, Q. Wang, M. Lundstrom and H. Dai, *Nature* **424**, 654 (2003).
8. X. Duan, Y. Huang and C. M. Lieber, *Nano Lett.* **2**, 487 (2002).
9. C. Li, W. Fan, D. A. Straus, B. Lei, S. Asano, D. Zhang, J. Han, M. Meyyappan and C. Zhou, *J. Am. Chem. Soc.* **108**, 9646 (2004).
10. B. Ricco, G. Torelli, M. Lanzoni, A. Manstretta, H. E. Maes, D. Montanari, and A. Modelli, *Proc. IEEE* **86**, 2399 (1998).
11. W. Kim, A. Javey, O. Vermesh, Q. Wang, Y. Li and H. Dai, *Nano Lett.* **3**, 193 (2003).
12. U. Ganguly, E. Kan, Zhang, Y., *Appl. Phys. Lett.* **87**, 043108 (2005); W. B. Choi, S. Chae, E. Bae, J.-W. Lee, B.-H. Cheong, J.-R. Kim and J.J. Kim, *Appl. Phys. Lett.* **82**, 275 (2003).
13. J. Guo, E. Kan, U. Ganguly and Y. Zhang, *J. App. Physics* **99**, 1 (2006) accepted 02/22/2006
14. J. De Blauwe, M. Ostraat, M. Green, G. Weber, T. Sorsch, A. Kerber, F. Klemens, R. Cirelli, E. Ferry, J. Grazul, F. Baumann, Y. Kim, W. Mansfield, J. Bude, J. Lee, S. Hillenius, R. Flagan and H. Atwater, *IEDM Tech. Dig.* **683** (2000).
15. G. Molas, B. De Salvo, G. Ghibaudo, D. Mariolle, A. Toffoli, N. Buffet, R. Puglisi, S. Lombardo and S. Deleonibus, *IEEE Trans. Nanotech.* **3**, 42 (2004).
16. D. Kim, T. Kim and S. K. Banerjee, *IEEE Trans. Electron Devices* **50**, 1823 (2003).

### Probing Electronic Properties of dendritic Ruthenium Complex bound to Single Walled Carbon Nanotubes

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## ABSTRACT

We have functionalized single walled carbon nanotubes (SWNTs) using ruthenium centered organometallic supramolecular dendritic complexes. These dendrimers have multiple binding sites with chemically specified chirality. Most importantly, they are mechanically rigid. We have fabricated field effect transistors (FET) using these functionalized SWNTs. Devices were processed with standard optical lithography and high resolution e-beam lithography. We are using FET response of these devices to study charge injection into the nanotubes and the resultant effect on the tube's transport properties. Organometallic based molecular adsorbents onto the nanotubes effect the transistor response. These functionalized tubes change their majority carriers from holes to electrons in these FETs. We believe this is due to charge transfer from the metal center through the ligand and finally onto the nanotube. This results in the potential for optically altering the carrier density, and therefore the transport properties of the nanotubes.

## INTRODUCTION

Since their discovery<sup>1</sup>, single walled carbon nanotubes have been regarded as important materials for future molecular devices. The exceptional mechanical, electronic and Opto-electronic characteristics<sup>2</sup> of SWNTs make them important materials for future nanodevices. SWNTs have been fabricated into field effect transistors<sup>3-4</sup>. The field effect transistor response<sup>5</sup> of the SWNT devices has been fairly well documented. Functionalization of SWNTs using various polymers<sup>6</sup>, nucleic acid<sup>7</sup> have been shown. We have functionalized SWNTs using ruthenium dendrimers. These dendrimers have multiple binding sites with chemically specified chirality. They are mechanically rigid, planar and are excellent optical absorbers. This enables the multidimensional constraints, geometry, required for advanced electronic, and optoelectronic devices. We have used the field effect transistor to probe the electronic properties of these functionalized SWNTs. FET response of these functionalized SWNTs have shown distinct characteristic variance as compare to pristine SWNTs. The variance is consistent with our proposed model.

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