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Nonvolatile Memory and Programmable Logic from Molecule-Gated Nanowires

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ABSTRACT

Bistable nanoscale switches have been assembled using nanowires and redox active molecules as building blocks. The nanodevices consist of nanowire field-effect transistors (NW-FET) functionalized with redox active molecules, where the redox species can store charges and thereby maintain the NW-FETs in either a logic *on* or *off* state with high or low channel conductance, respectively. Single NW and crossed NW-FET devices have been assembled and shown to switch reversibly as two- and three-terminal devices. Individual NW devices with *on*/*off* ratios exceeding 10^4 and retention times in excess of 20 min, and integrated arrays in which devices are independently addressable, have been assembled. The characteristics of the molecule-gated NW-FET devices suggest that they could serve as key elements in a range of nanoelectronics applications, including nonvolatile memory and programmable logic array.

The exponential advances in device integration observed over the past several decades in microelectronics may soon end due to fundamental physical and/or economic limitations.[1,2] This prediction has motivated extensive efforts aimed at developing new device concepts and fabrication approaches that may enable integration to go far beyond the limits of conventional microelectronics technology.[3,4] Bottom-up assembly of well-defined nanoscale building blocks, such as molecules,[5−7] quantum dots,[8] and nanowires (NWs),[3] having key properties controlled by size, morphology, and chemical composition, represents a powerful approach that could overcome these limitations. For example, NWs and carbon nanotubes have been used to construct a number of functional devices and device arrays, including field effect transistors (FETs),[9−12] p−n diodes,[10,12,13] bipolar junction transistors,[13] and integrated logic circuits.[14−16] These results represent important advances for nanoelectronics, yet the development of nanostructures exhibiting new device function could open up additional and potentially unexpected opportunities for nanoelectronics systems.

To address the issue of creating new functional devices, we have been exploring the combination of NWs and molecular building blocks and herein report bistable nanoscale switches assembled using semiconductor NWs and redox active molecules as building blocks. The nanodevices consist of NW-FETs functionalized with redox active molecules, where the redox species can store charges and thereby maintain NW-FETs in either a logic *on* or *off* state. Single NW and crossed NW-FET devices have been assembled and shown to switch reversibly as two- and three-terminal devices. Individual NW devices with *on*/*off* ratios exceeding 10^4 and retention times in excess of 20 min, and integrated arrays in which devices are independently addressable, have been assembled.

The overall configuration and operating principle of our NW devices are illustrated in Figure 1. In a NW-FET functionalized with redox active molecules, an applied gate voltage (V_g) or source-drain voltage (V_{sd}) pulse injects net positive or negative charges on the molecular layer. The oxide layer on the NW surface, which can be controlled synthetically, serves as a barrier to reduce charge leakage between the molecules and NW, and thus maintain the charge state of the redox molecules. The charged redox molecules gate the NW-FET to a logic *on* state with higher channel conductance or logic *off* state with lower channel conductance. For example, positive charges, like a positive gate, will lead to accumulation of electrons and an *on* state in n-channel NW-FETs, and depletion of holes and an *off* state in p-channel NW-FETs.

The NWs used in this study include p-type Si, n-type InP, and n-type GaN, with diameters ranging from 10 to 30 nm. The NWs were synthesized using reported methods,[17] and NW-FETs were fabricated using procedures described previously.[9−11] Several different redox active molecules were examined including ferrocene, zinc tetrabenzoporphine, and cobalt phthalocyanine (CoPc). Below we focus our discussion on n-channel InP NW-FETs functionalized with CoPc redox molecules, although similar results consistent with the model presented in Figure 1 were obtained for the different NWs and redox molecules. The NW-FETs were functionalized by spin coating chlorobenzene solutions of CoPc, which pro-

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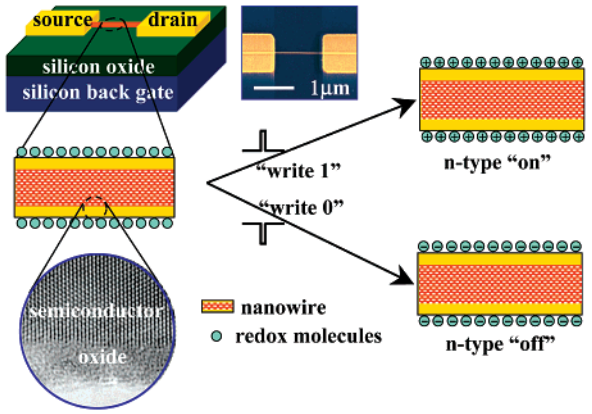

Figure 1. (a) NW-based nonvolatile devices. The devices consist of a semiconductor NW configured as a FET with the oxide surface functionalized with redox active molecules. The top-middle inset shows an SEM image of a device, and the lower circular inset shows a TEM image of an InP NW highlighting the crystalline core and surface oxide. Positive or negative charges are injected into and stored in the redox molecules with an applied gate or bias voltage pulse. In an n-type NW, positive charges create an *on* or logic "1" state, while negative charges produce an *off* or logic "0" state.

duces a uniform layer of CoPc on NW surfaces with layer thicknesses greater than one monolayer. Typical conductance, $G = I/V_{sd}$ (I is current), vs V_g data for an n-InP NW-FET before and after modification with a CoPc layer are shown in Figure 2a. Before addition of the CoPc layer, the response is characteristic of an n-type FET; that is, little or no hysteresis is observed in $G-V_g$ for positive/negative variations in V_g. Significantly, a large hysteresis in $G-V_g$ is reproducibly observed after the NW surface is modified with CoPc (red curve, Figure 2a). As V_g is increased from negative to positive, the channel conductance increases at a more negative value than for the unmodified NW, and as V_g is then cycled to negative values the channel conductance decreases at a more positive value than in the unmodified NW. The hysteresis defines the two states of a bistable system and has been exploited to configure a three-terminal switch or memory device. The low conductance *off* state and high conductance *on* state of the NW-FET switch are continuously monitored by measuring G at a fixed V_{sd} and V_g, while the NW-FET is switched between *on* and *off* states by a V_g pulse (e.g., ±10 V). A typical CoPc-modified NW FET operated in this way (Figure 2b) shows reversible switching over many cycles between the *on* and *off* states, with the conductance change of nearly 10^4 (i.e., from 600 to <0.1 nS) being maintained for at least 100 cycles. Similar results have been obtained on more than 80 devices.

The three-terminal devices demonstrate that the molecule-gated NW-FETs can function as bistable *on*/*off* switches, although the operation of these devices with the global back gate (substrate) precludes the assembly of integrated and individually addressable device arrays. To overcome this important limitation, we have investigated the possibility of switching devices in a two-terminal configuration, where a V_{sd} pulse is used to inject positive or negative charges on the redox active molecules. Current (or G) vs V_{sd} measurements exhibit a large hysteresis in CoPc-modified NW-FETs

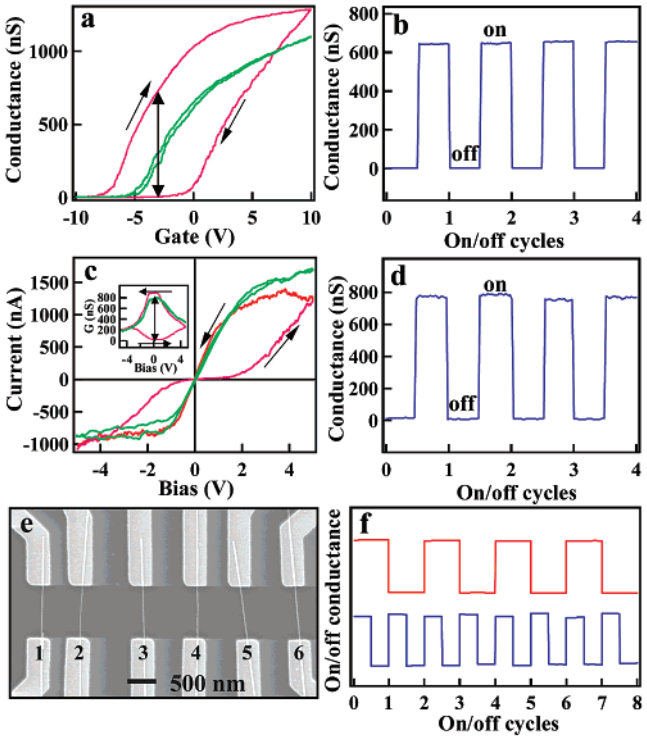

Figure 2. (a) G vs V_g for an n-InP NW-FET before (green) and after (red) surface modification with CoPc recorded with V_{sd} = 0.1 V. Single-headed arrows show gate sweep directions, and the double-headed arrow indicates a position of large *on*/*off* hysteresis, which can be explained as follows: At negative back-gate the NW band is raised, which depletes carriers in the n-type NW and can oxidize redox molecules. The positively charged molecules act effectively as a compensating positive gate, and hence the NW-FET can be turned on at a more negative back-gate voltage than the unmodified NW. The converse is true at high positive back gate, which enables the modified NW to be turned off at a more positive back-gate voltage. (b) Reversible *on* and *off* switching of the device in (a) using +10 and −10 V, respectively, 1 s gate pulses; *on*/*off* states were measured with V_{sd} = 0.1 V and V_g = −3 V. (c) I vs V_{sd} for an n-InP NW-FET before (green) and after (red) surface modification with CoPc; (inset) G versus V_{sd}. Single-headed arrows show bias sweep directions, and the double-headed arrow (inset) indicates the position of maximum hysteresis. (d) *On* and *off* switching of the device in (c) using +5 and −5 V, respectively, 1 s bias pulses; *on*/*off* states were measured with V_{sd} = 0.1 V. (e) SEM image of a parallel array of NW devices. (f) Independent switching of two devices in a parallel array; +5 and −5 V bias pulses were used to switch between *on* and *off* states, respectively.

(Figure 2c), while no hysteresis is observed in the unmodified NW-FETs. Similar to our studies of three-terminal devices, we find that it is possible to reversibly switch between *on*/*off* states using 2−5 V pulses (Figure 2d). Typically, we find that devices can be switched at least 60 times before any degradation in *on*/*off* ratio is observed; the retention time within the *on* and *off* states is addressed below.

The ability to assemble reproducibly two-terminal bistable switch elements could enable individually addressable integrated arrays of parallel NW devices in two-dimensions or even in three-dimensions. To this end, we have assembled and characterized parallel arrays of CoPc-modified NW-FETs. Parallel arrays of NW devices are readily assembled using the fluidic-flow directed assembly approach (Figure

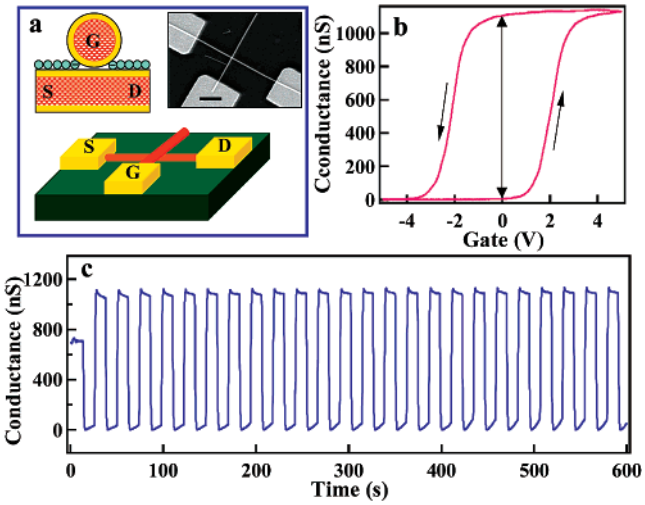

Figure 3. (a) Schematic of a cNW-FET nonvolatile device where one NW is used as the gate (G) and the other NW is the active element. The charge state of the redox molecules on the NW surface is changed only in the vicinity of the gate (left inset). (inset) SEM image of a device; scale bar is 1 μm. (b) G vs NW V_g for a cNW-FET modified with CoPc. Single-headed arrows indicate the NW V_g sweep direction, and the double-ended arrow indicates the position of large hysteresis. (c) Real-time switching of the device between on and off states using +5 and −5 V, respectively, V_g pulses.

2e).[18] Independent addressing and switching of parallel NW devices were tested by simultaneously measuring the characteristics of two adjacent elements. Significantly, we find that the two adjacent two-terminal devices can be independently switched between *on* and *off* states with no significant coupling observed either during switching or reading (Figure 2f). These results demonstrate that the molecule-gated NW-FET switches can be independently addressed, and thus could be utilized, for example, as nonvolatile random access memory that is integrated in parallel array structures.

The parallel array structure of molecule-gated NW-FET devices takes advantage of the small, ∼10 nm diameters of the NWs, although the much longer FET channel length (i.e., the length of the NW between source−drain contacts) reduces the ultimate potential for integration in two-dimensions. However, we have recently reported an alternative configuration for integrated NW-FETs in which crossed NWs are used both as the FET channels and the gates.[14] The crossed NW-FET (cNW-FET) structure enables much more efficient integration since the channel length is defined in large part by the gate NW diameter, and moreover, the key nanoscale integration is determined by assembly not lithography.[14] We have extended this new concept to the case of molecule-gated NW devices (Figure 3a), where the *on*/*off* states of the active NW-FET are switched using a voltage pulse applied to the gate NW. Plots of G vs NW-V_g for a CoPc-modified cNW-FET exhibit large hysteresis (Figure 3b) and thus suggest that bistable switches are also possible using the cNW-FET configuration. Significantly, we find that the CoPc-modified cNW-FETs can be switched reversibly between *on* and *off* states using +5 and −5 V pulses, respectively, and that the switching can be continued for hundreds of cycles without any significant change in the *on*/*off* conductance ratio (Figure 3c). Although additional work will be required to define the mechanism, we suggest that the cNW gate injects charge directly into "gate" molecules adjacent to this NW (inset, Figure 3a). This model implies that bistable switch elements can be integrated at a density approaching that of the cNW gate diameter, although future studies of integrated structures will be required to define clearly this key property.

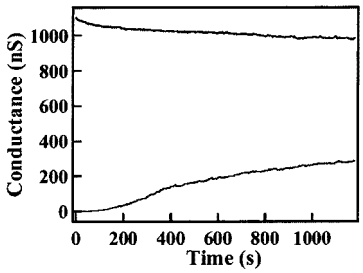

Figure 4. Retention times for a CoPc-modified cNW-FET device. Red and green curves show G vs time after the device was switched *on* and *off*, respectively.

To address whether these bistable switches can be utilized as nonvolatile memory or programmable logic elements, we have characterized the device retention times. Figure 4 shows plots of G vs time for a CoPc-modified cNW-FET device in both the *on* (red line) and *off* (green line) states. The initial *on* (>1000 nS)/*off* (<0.1 nS) ratio exceeds 10^4 but decays slowly to a steady state difference of ca. 700 nS. Significantly, this difference in G is maintained for at least 20 min, and thus the retention times are comparable to or longer than recently reported molecular memory structures.[6] Measurements on over 50 devices, including cNW-FET, and three-terminal and two-terminal single wire structures, show similar retention times with some devices holding state for many hours. We believe that variability in the retention time is likely due to variations in the barrier separating an active NW core and the redox active molecules, and we suggest that further studies of this barrier (e.g., thickness) should enable a better understanding of charge leakage and the creation of longer retention time devices. Last, to test the importance of redox active molecules in charge storage, we have also carried out similar experiments in which NW-FETs were functionalized with poly(methyl methacrylate). Switching was observed with this dielectric, although the typical retention times were seconds versus 10's of minutes to hours for the redox active molecular layers. These results suggest strongly that redox active molecules are critical for efficient charge storage and nonvolatility in our NW devices.

In summary, bistable nanoscale switches consisting of nanowire field-effect transistors (NW-FET) functionalized with redox active molecules have been assembled. Parallel NW-FET and cNW-FET devices were shown to switch reversibly as two- and three-terminal devices. Individual NW devices with *on*/*off* ratios exceeding 10^4 and retention times in excess of 20 min, and integrated arrays in which devices are independently addressable, were also characterized. The unique properties (long retention time and large on/off ratio) of the molecule-gated NW-FET devices make them attractive elements not only for nonvolatile memory but also program-

mable logic arrays. Last and unlike conventional planar electronics, these NW-based bistable switches can be easily assembled in a layer-by-layer fashion that could be extended to integration in three-dimensional (3D) space, which would expand overall device density dramatically beyond the current technology road map.

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