

Molecular random access memory cell

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Electronically programmable memory devices utilizing molecular self-assembled monolayers are reported. The devices exhibit electronically programmable and erasable memory bits compatible with conventional threshold levels and a memory cell applicable to a random access memory is demonstrated. Bit retention times >15 min have been observed. © 2001 American Institute of Physics. [DOI: 10.1063/1.1377042]

The programmable storage of digital information as packets of charge is beginning to reach not only technological but fundamental limits. Electronic memories that operate at the charge limit (e.g., by single electron effects) have been demonstrated,^{1,2} but have not yet addressed the dimensional limit, i.e., a single molecule. Although memory phenomena have been studied in bulk organic materials (such as organometallic charge-transfer complex salts^{3,4}) and thermally deposited thin films by scanning tunneling microscopy (STM),⁵ we demonstrate here charge storage in a self-assembled nanoscale molecular device (1) that is operated as a random access memory, (2) with practical thresholds and output under ambient operation, (3) with bit retention times >10 min, and (4) with the potential to be scaled to the single-molecule level.

Figure 1 shows the molecules used in this study and the operation principle of the memory. The devices consist of a nanoscale (30–50 nm diameter) area of a self-assembled monolayer contacted on both ends by metallic contacts, using a method previously reported.^{6,7} The four systems studied were: Au–(1)–Au (1: 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1-benzenethiolate); Au–(2)–Au (2: 4-ethynylphenyl-4'-ethynylphenyl-2'-nitro-1-benzenethiolate); Au–(3)–Au (3: 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-1-benzenethiolate) [Fig. 1(a)]; as well as Au–(4)–Au (4: 4-ethynylphenyl-4'-ethynylphenyl-1-benzenethiolate) that had neither the nitro or amine functionalities (structure not shown). The memory device operates by the storage of a high or low conductivity state. Figure 1(b) shows the write, read, and erase sequence for (1). An initially low conductivity state (low σ) is changed (written) into a high conductivity state (high σ) upon application of a voltage pulse. The direction of current that flows during this "write" pulse is diagrammed. The high σ state persists as a stored "bit", which is unaffected by successive read pulses.

Molecules with the nitro moieties (1 and 2) are observed to change conductivity state, whereas the amine only (3) and the unfunctionalized molecule (4) do not exhibit storage. We first describe the characteristics obtained by linear voltage sweeps [current (voltage) $I(V)$ characteristics], then demonstrate the same effects (and circuit) using voltage pulses.

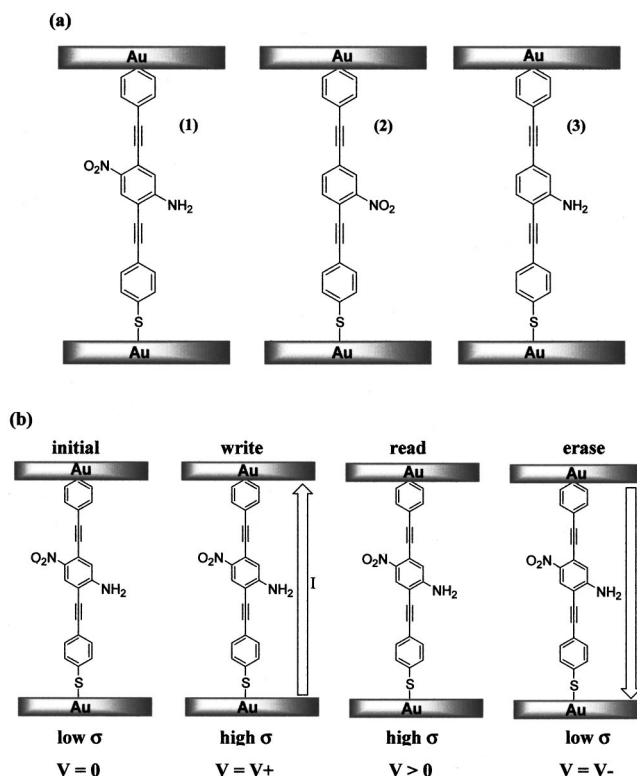


FIG. 1. The configuration of the molecular devices and the operation principle of the storage and memory. Approximately 1000 molecules are sandwiched between Au contacts formed by a chemisorbed thiol/Au contact on bottom and an evaporated Au contact on top. The entire active region has a diameter of 30–50 nm. (a), The molecules (1–3) used in this study. Another molecular system that had neither the nitro or amine functionalities was also studied (not shown). (b), The memory device operates by the storage of a high or low conductivity state. An initially low conductivity state (low σ) is changed into a high conductivity state (high σ) upon application of a voltage. The direction of current that flows during the write and erase pulses are diagrammed by the arrows. The high σ state persists as a stored bit.

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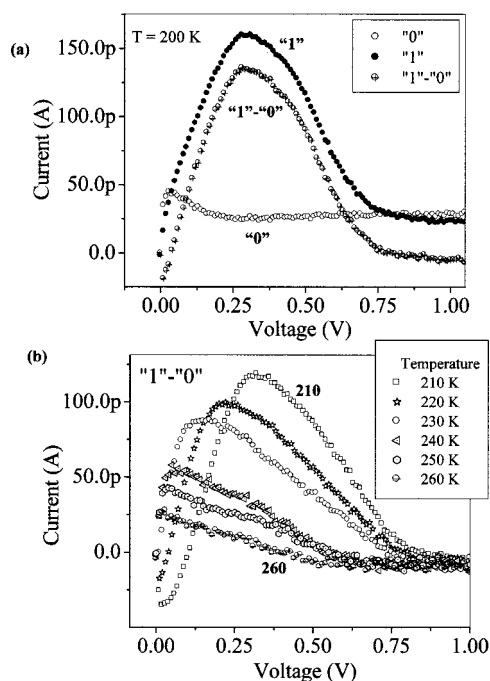


FIG. 2. $I(V)$ characteristics of a Au-(1)-Au device. (a) The device at 200 K. 0 denotes the initial state, 1 the stored written state, and 1-0 the difference of the two states. Positive bias corresponds to hole injection from the chemisorbed thiol-Au contact. (b) Difference curves (1-0) as a function of temperature.

Figure 2(a) shows the $I(V)$ characteristics⁸ of a Au-(1)-Au device at 200 K initially (defined as "0") and after (defined as "1") a write pulse, as well as the difference between the two (defined as 1-0). Positive bias corresponds to hole injection from the chemisorbed thiol-Au contact (the bottom in Fig. 1, not the top evaporated Au contact). The device initially probed with a positive voltage exhibits a low conductivity state. Subsequent positive sweeps show a high conductivity state with $I(V)$ characteristics identical to the previous values (1). Device bias swept in the reverse bias direction causes the $I(V)$ to be identically reset to the initial, 0 $I(V)$ characteristic. The characteristics are repeatable to high accuracy and device degradation is not observed. This ability to program, read, and refresh the state of the molecular device accomplishes the functionality of a random access memory (RAM). Figure 2(b) shows the difference characteristic (1-0) of (1) as a function of temperature.

A characteristic bit retention time was obtained by measuring the stored high conductivity state at various times intervals after programming the Au-(1)-Au device. After an initial write bias sweep, the peak current of the stored state 1 exhibits an exponential decay with a time constant (τ) of approximately 800 s at 260 K [Fig. 3(a)]. Measurements of the retention time at different temperatures yields an exponential dependence with $1/T$, indicating an activated behavior [Fig. 3(b)]: $\tau = \tau_0 \exp(E_a/kT)$. The activation energy E_a for this molecule over this bias regime was found to be approximately 80 meV.

Memory effects were also observed in devices with the molecules having only the nitro moiety (2), although in this case the storage was of a low conductivity state, opposite to that of molecule (1). Figure 4 demonstrates the storage of this state in molecule (2) at (a) 60 K and (b) ambient temperature (300 K). The setpoints indicated are the operating points for the circuit of Fig. 5.

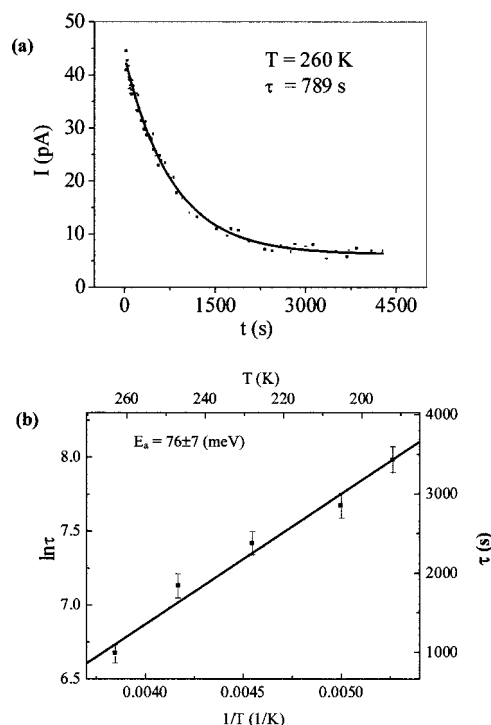


FIG. 3. Bit retention as a function of time and temperature. (a) Bit retention for (1) exhibits an exponential decay with a time constant (τ) of 790 s at 260 K. (b) Temperature dependence of τ gives an activation energy $E_a = 76 \pm 7$ meV.

perature, 300 K. The time constant for this molecule was measured to be 910 s (>15 min) at 300 K. The window over which the 0 and 1 differ by a constant amount of ~ 150 pA is nearly 5 V, providing well-separated thresholds. Subsequent reads and resets identically recovered the $I(V)$ characteris-

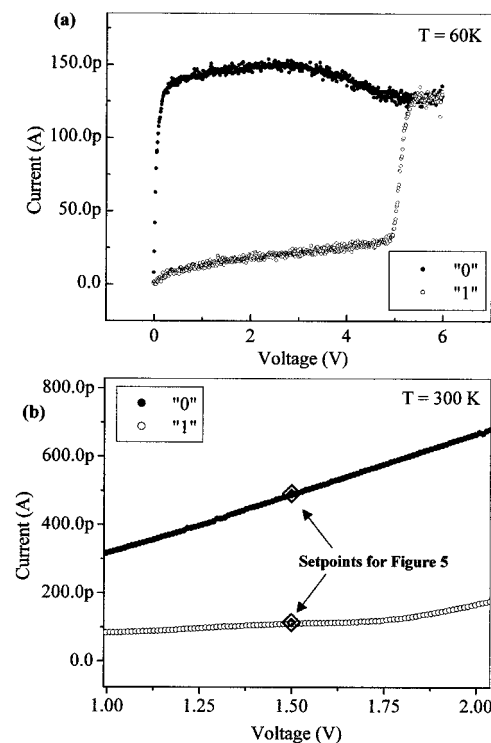


FIG. 4. $I(V)$ characteristics of stored and initial/erased states in Au-(2)-Au at (a) 60 K and (b) ambient temperature (300 K). The setpoints indicated are the operating points for the circuit of Fig. 5.

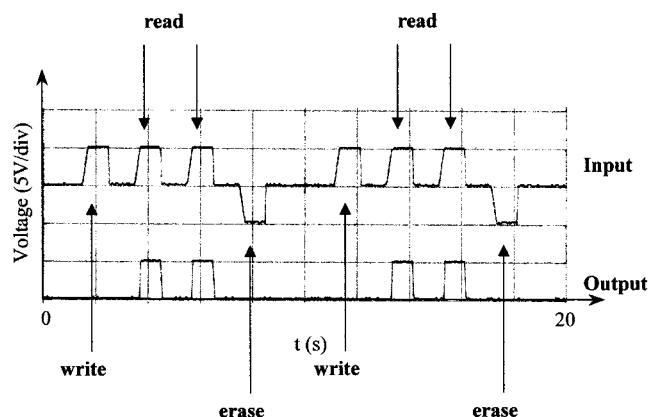


FIG. 5. Measured logic diagram of the molecular random access memory.

tics. At 300 K, thermal activation does contribute some non-zero current, although the thresholds are still well separated (between 200 and 500 pA). The details of the mechanism that causes a high conductivity state in (1) and a low conductivity state in (2) are presently under investigation.

Figure 5 is a measured logic diagram demonstrating a RAM cell using these devices [specifically, molecule (2)] at ambient temperature. To convert the stored conductivity to standard voltage conventions, the output of the device was dropped across a resistor, sent to a comparator [set at the points diagrammed in Fig. 4(b)], and inverted and gated with the read pulse. The upper trace shown in Fig. 5 is an input wave form applied to the device, and the lower is the RAM cell output. The first positive pulse configures the state of the cell by writing a bit, and the second and third positive pulses read the cell. The third pulse (and subsequent read pulses) demonstrates that the cell is robust and holds the state up to the limit of the bit retention time. The negative pulse erases the bit, resetting the cell. The second set of four pulses repeats this pattern, and many hours of continuous operation

have been observed with no degradation in performance. The operating speed of the device is limited by the RC time constant, which can be improved by varying functional end-groups to increase current density.^{6,9} Recent, similar STM work¹⁰ demonstrated operating speeds of 80 ns.

The present devices utilize nanoscale structures that constrain the number of molecules in the active region to a few thousand which is determined by lithographic limitations in defining the contacts. There are no indications in the characteristics observed in this study that limitations exist for scaling the number of molecules in the active region of the device to one, assuming that an appropriate fabrication scheme can be identified.

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