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Nanoscale Reversible Mass Transport for Archival Memory

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ABSTRACT

We report on a simple electromechanical memory device in which an iron nanoparticle shuttle is controllably positioned within a hollow nanotube channel. The shuttle can be moved reversibly via an electrical write signal and can be positioned with nanoscale precision. The position of the shuttle can be read out directly via a blind resistance read measurement, allowing application as a nonvolatile memory element with potentially hundreds of memory states per device. The shuttle memory has application for archival storage, with information density as high as 10^{12} bits/in^2, and thermodynamic stability in excess of one billion years.

The miniaturization of nonvolatile silicon-based memory devices has revolutionized the creation, access, and exchange of digital information. There are tremendous benefits in continuing this miniaturization into the nanoscale. Unfortunately, a general trend for memory storage, independent of medium, is decreasing lifetime with increasing memory density. For example, stone carvings in the Karnak Temple in Luxor at an approximate density of 2 bits/in^2 are largely readable after 3800 years, while information written with individual atoms by scanning tunneling microscopy manipulation[1] at a density of ~100 Tbits/in^2 has an estimated lifetime of only 10 ps at room temperature. Conventional digital memory configurations in use today, with densities of order 10−100 Gbits/in^2, have an estimated lifetime of only 10−30 years.[2] Interestingly, the Domesday Book, the great survey of England commissioned by William the Conqueror in 1086 and written on vellum, has survived over 900 years, while the 1986 BBC Domesday Project, a multimedia survey marking the 900th anniversary of the original Book, required migration from the original high-density laserdiscs within 2 decades because of media failure.[3]

We here describe a robust memory device, nanomechanical in nature, with an estimated configurable density more than 1 Tbits/in^2 and with thermodynamic stability at room temperature in excess of one billion years. The memory unit can be written to and read out using two-terminal electrical leads operated at low voltages, facilitating large-scale integration, and is easily incorporated into conventional silicon processing. The nanomechanical system is naturally hermetically sealed and thus provides its own protection against environmental contamination.

Figure 1a shows a schematic of our memory device. The primary element is a nanoparticle encapsulated within a multiwall carbon nanotube. The nanoparticle can shuttle back and forth within the nanotube channel and the physical location of the particle defines the logic state. We note that different nanomechanical memory geometries have been previously examined,[4−6] including a proposal (yet to be realized) for an encapsulated fullerene shuttling within a nanotube core.[7] The key challenges to physically realizing and operating the shuttle memory of Figure 1a are reliable construction of the device, a means to "write" to it (i.e., translate the shuttle), and a means to nondestructively "read" it, (i.e., nonperturbatively determine the position of the shuttle without reliance on cumbersome methods such as transmission electron microscopy). Furthermore, for the memory to be useful, long-term stability with overwriting must be possible. Studies of electromigration-driven mass transport on or in nanotubes[8−12] suggest that transition metal nanoparticles may be good candidates for such a shuttle.

We synthesize the required heterogeneous nanostructure consisting of a nanotube with an enclosed iron nanoparticle shuttle in a single step via pyrolysis of ferrocene in argon at 1000 °C. The nanotube memory elements are then ultrasonically dispersed in isopropanol and deposited on a substrate.

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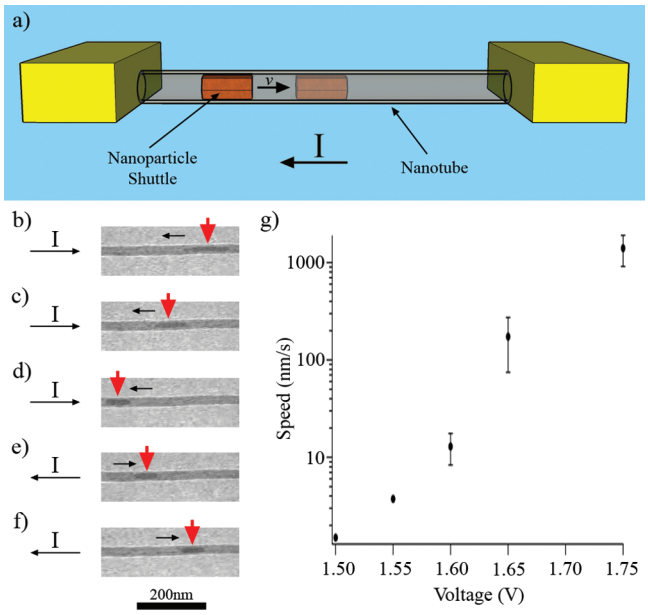

Figure 1. Nanoshuttle memory device. (a) An artistic representation of the memory device shows a nanoparticle shuttle encapsulated within a MWCNT. Bias applied between electrical contacts is increased until a onset current on the order of a few hundred microamperes is reached, causing the nanoparticle to move in a direction opposite the applied current. (b−f) TEM images of the shuttle moving under applied bias over a distance of ∼200 nm. The contacts are out of the field of view to the left and right. (b−d) The current is applied to the right, and the nanoparticle moves to the left. (e, f) The current is reversed, and the particle returns to its original position. The shuttle can be moved across the entire length of the nanotube in a reversible and reproducible fashion. This process can be repeated over multiple iterations, as shown in the supplementary movie (Supporting Information). (g) Adjusting the applied bias strongly affects the speed of the nanoparticle shuttle. The speed is shown plotted versus the bias. The highest speed measured (not shown) is limited by the frame rate of our video camera and is greater than 25 μm/s.

For diagnostic purposes, we use a custom fabricated silicon nitride membrane compatible with transmission electron microscopy (TEM) as a substrate. The devices are created in one lithographic step; electrical contacts are patterned on the ends of the nanotube and 100 nm of palladium is deposited and lifted off in acetone. The planar devices on the membrane are then mounted inside a TEM biasing stage allowing high-resolution imaging in real time during device operation.

Figure 1b−f shows a series of transmission electron microscopy (TEM) images of the nanotube with an enclosed shuttle. The electrical contacts at the ends of the nanotube are outside the field of view. Upon application of an electrical current through the nanotube, the shuttle moves via electromigration forces.[12] TEM observation indicates that the iron nanoparticle is crystalline throughout the shuttling process. As the current direction is reversed, the direction of motion for the shuttle is reversed.[13] Dropping the current to zero rapidly quenches the shuttle motion, "freezing" its position. Although mass transport on or inside nanotubes has been previously described for a variety of metals,[8−12] this is, to our knowledge, the first demonstration of precision controllable, fully reversible, long-range solid state mass transport within a nanotube.

The speed of the shuttle can be tuned over several orders of magnitude by varying the applied bias voltage V, as shown in Figure 1g. Just beyond a threshold for the onset of motion at $V \sim 1.55$ V, the shuttle moves at a rate of ∼1 nm/s, on the order of the speed of slow continental drift,[14] while at $V = 1.75$ V, the highest bias applied to this device, the shuttle moves at 1.4 μm/s, comparable to the speed of the motor protein myosin.[15] With other devices we have observed that the shuttle velocity can be increased by at least 4 orders of magnitude beyond this, exceeding 2.5 cm/s, the maximum speed we can detect at high magnification due to the frame rate of our TEM video camera. The true top speed could be considerably higher.

In addition to continuously translating the shuttle, the shuttle motion can be precisely "stepped". Application of a short (∼20 ns) voltage pulse on the order of 2 V causes the shuttle to translate 3 nm (see movie in Supporting Information). Successive pulses induce successive translations analogous to, but an order of magnitude more precise than, the walking motion of myosin VI, which moves in 36 nm steps along an actin filament.[16] The combination of static biasing and pulsing allows precision control of the shuttle position from the micro- to the nanoscale. We note that the shuttle motion is dictated strictly by the applied dc bias, irrespective of the presence or absence of the TEM imaging electron beam.

The different shuttle position states, as shown in Figure 2b, clearly serve as digital memory. If we define positions left of image center as "0" and right of image center as "1", then a desired logic state can be written by application of a voltage pulse, of suitable polarity and sufficient duration, which physically positions the shuttle. The written state can be read out via TEM imaging, as shown in Figure 2a.

While interesting from a diagnostic point of view, using TEM to read out the state of the device is clearly impractical. Most desirable would be a simple two-terminal electrical readout. We find that the axial electrical resistance of the nanotube is sensitive to the physical location of the enclosed nanoparticle shuttle. In Figure 2b, we show the nanotube resistance R as the shuttle is continuously repositioned.[17] Although some noise is apparent, Figure 2a demonstrates that R tracks the TEM-determined position coordinate remarkably well. With the discrimination similar to that used for TEM positioning, the logic states are thus faithfully read out from blind resistance measurements alone.

Importantly, probing the state of the system via small voltage pulses is nonperturbative and does not alter the shuttle position; hence the memory electrical readout is nondestructive. This is demonstrated in Figure 3, where the states 101010 have been sequentially written to the device and read out in succession four times for each written state. Both the TEM-determined position state and the resistively determined state are in agreement, with no state destruction cause by readout. Due to the two-terminal configuration, such memory devices could be scaled to produce memory densities ∼1 Tbit/in^2, greater than current state of the art hard drive

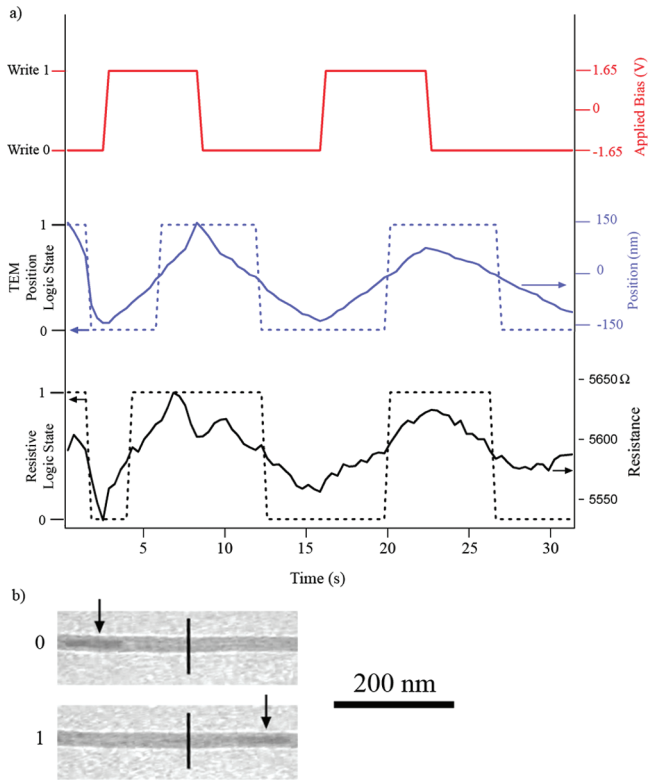

Figure 2. Writing to and readout of the memory device. The state of the memory device can be determined by either direct TEM observation of the position or by measuring the resistance. (a) The graph shows the write signal (top red line). Application of a right-directed current causes the shuttle to move left, creating a "0" state. Subsequent application of a left-directed current causes the shuttle to move right, creating a "1" state. The middle solid line (blue) is the TEM measured position of the nanoparticle. The overlaying dashed line (blue) is the measured memory state based on the position. Similarly, the bottom solid and dashed (black) lines show electrical readout of the memory state. (b) TEM image of the device in the "0" and "1" states. The arrows identify the nanoparticle position. The solid line is the threshold between states.

storage, with memory density ~200 Gbit/in^2. The shuttle memory density could be increased by another order of magnitude or more by applying multiple thresholds to store many states per device.

The unique geometry afforded by the encapsulated shuttle naturally yields a hermetically sealed system, immune to environmental contamination. In contrast to conventional memories, which may suffer from interaction between magnetic domains as well as material breakdown, the information in the shuttle memory is only compromised if the shuttle moves. We now turn to an examination of the readout mechanism and the expected lifetime of the memory device and written state.

The readout mechanism is tied to the electrical resistance of a multiwall nanotube, which is itself a subject of much speculation and controversy.[18−21] Our experiments demonstrate that the iron shuttle, despite residing entirely within the core of the nanotube, serves as a position-dependent scattering center. In a model of on-tube transport with intershell coupling, the shuttle could locally alter intershell coupling as well as influence quantum interference of

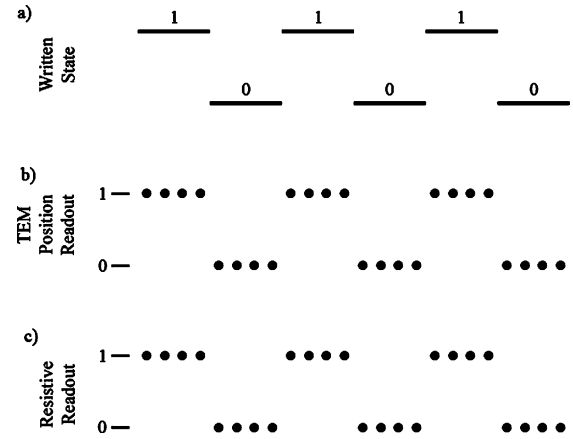

Figure 3. Sequential reading and writing. (a) The states 101010 are written sequentially into the memory device. TEM readout of the shuttle position (b) and the device resistance (c) yield the written states, 101010. Multiple readouts of the same state demonstrate nondestructive readout. Writing voltage: ±1.6 V. Resistance discrimination levels: >5620 Ω "1" and <5580 Ω "0". TEM-determined position discrimination levels ±50 nm for "1" and "0", respectively.

electron wave functions along the tube. If the electronic transport is diffusive, the system may be in part modeled as regions of materials with different resistivities. Position dependence in the total resistance could then come from spatial variations in the resistivity of the nanotube (caused by defects) or simply by geometric effects. If the transport is in the ballistic regime over limited segments, local resistance changes could be due to electron resonance effects.

Irrespective of the details of the electron conduction mechanism along the nanotube, we model the transport of the shuttle under electromigration as occurring within a biased sawtooth potential with thermally activated hops between local minima separated by a distance L, assuming rapid equilibration within each local minimum. The unbiased (i.e., $V = 0$) barrier between minima is ΔE; the attempt rate is ω; the voltage across the nanotube is V. The length of the nanotube is D, so V/D is the average electric field. The shuttle speed is then

$$v \sim \omega L e^{-(\Delta E - (1/2)Q_{\mathrm{eff}}V(L/D)/kT} \quad (1)$$

where the effective charge Q_{eff} measures the strength of the coupling between the shuttle and the external electric field. Since Q_{eff} embodies not just the direct coupling of charge to the local electric field[22] but also any effect of charge carrier scattering events, it cannot be directly identified with the total charge on the shuttle. For structurally well-ordered nanotube walls, the order-of-magnitude distance L for a rigid shuttle is bounded below by the body center cubic (bcc) iron or graphenic lattice constant, both on the order of 2 Å, since this sets the repeat distance for axial (achiral) or helical (chiral) motions. For less-ordered nanotubes wherein motion of shuttles is pinned at structural imperfections, the characteristic step distance would be set by the separation between pinning sites; the ability experimentally to reduce the step size to ~3 nm sets an upper limit on the importance of such disorder. Finally, depending on the elastic relaxation of the shuttle, hopping events may involve motions of Frenkel−Kontorova domain walls that are internal to the iron shuttle.

The observed exponential dependence of the speed on the applied voltage (shown in Figure 1g), $d(\log_{10} v)/dV \sim 30$ V^{-1}, sets $Q_{eff}\, L/D \sim 1.5$ electron charges (independent of ΔE, ω, or kT). The attempt rate ω estimated from the center-of-mass vibration of the shuttle ($\sim 10^9$ s^{-1}) is smaller than is typical for molecular-scale hopping (10^{12} s^{-1}) since the shuttle is much heavier. However, the dependence of the barrier height on the attempt rate (and the step length) is only logarithmic.

The interface between a well-ordered nanotube inner wall and an incommensurate crystalline Fe nanoshuttle is expected to be relatively smooth, as required to obtain electromigratory motion at realistic currents, but nevertheless kinetic barriers against stick−slip motion can be large compared to room-temperature thermal energies,[23] as demonstrated by the lack of observable motion in the undriven system. Making a conservative assumption of room-temperature operation within the TEM, the measured shuttle speeds place a lower bound of $\Delta E \sim 1.5-1.7$ eV on the barrier height. Additional mechanisms for surmounting the kinetic barrier against motion, such as athermal fluctuations caused by electron scattering events or a rapid ballistic passage over multiple successive barriers under electromigration, would tend to increase the estimate for the barrier size and hence further stabilize the undriven system against purely thermal diffusive wandering. The precise value of the barrier, and the resulting shuttle speeds, may be sensitive to detailed structural parameters, such as the wrapping indices of the inner wall and the orientation of the Fe lattice with respect to the axis of the nanotube.

To determine the lifetime of the memory device, we consider the motion of the iron shuttle at room temperature and zero bias over an appreciable enough distance to cause loss of information (here, 200 nm). The estimated barrier then yields a room-temperature dwell time greater than 3.3×10^{17} s. Although truly archival storage is a global property of an entire memory system, the first inescapable requirement for such a system is that the underlying mechanism of information storage for individual bits must exhibit a persistence time much longer than the envisioned lifetime of the resulting device. A single bit lifetime in excess of a billion years demonstrates that this system has the potential to store information stably for any practical desired archival time scale. Thus, nanoscale electromechanical memory devices such as those described here present a new solution to ultrahigh density, archival data storage.

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Supporting Information Available: A video showing that the shuttle can be moved across the entire length of the nanotube in a reversible and reproducible fashion. This material is available free of charge via the Internet at http://pubs.acs.org.

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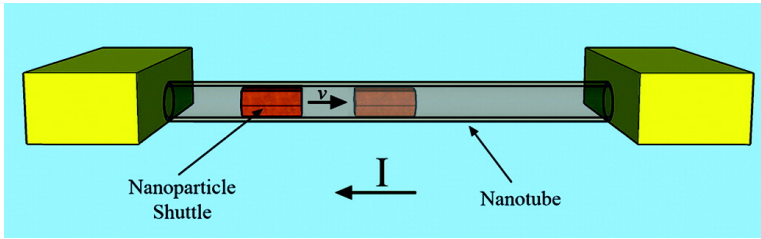

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