Carbon Nanotube–Based Nonvolatile Random Access Memory for Molecular Computing

Thomas Rueckes,† Kyoungha Kim,‡ Ernesto Joselevich,† Greg Y. Tseng,† Chin-Li Cheung,† Charles M. Lieber†,‡*

A concept for molecular electronics exploiting carbon nanotubes as both molecular device elements and molecular wires for reading and writing information was developed. Each device element is based on a suspended, crossed nanotube geometry that leads to bistable, electrostatically switchable ON/OFF states. The device elements are naturally addressable in large arrays by the carbon nanotube molecular wires making up the devices. These reversible, bistable device elements could be used to construct nonvolatile random access memory and logic function tables at an integration level approaching $10^{12}$ elements per square centimeter and an element operation frequency in excess of 100 gigahertz. The viability of this concept is demonstrated by detailed calculations and by the experimental realization of a reversible, bistable nanotube-based bit.

In the past several decades, there has been a nearly constant exponential growth in the capabilities of silicon-based microelectronics (1). However, it is unlikely that these advances will continue much into the new millennium, because fundamental physical limitations, which prevent current designs from functioning reliably at the nanometer scale, will be reached while at the same time exponentially rising fabrication costs will make it prohibitive to raise integration levels. Molecular electronics (2, 3) can in principle overcome these limitations of silicon technology, because it is possible to have single-molecule devices that are organized cheaply in parallel by self-assembly. Much effort in this area has been focused on organic molecules as device elements, with very recent demonstrations of irreversible switches (4) and large negative differential resistances (5) for ensembles of molecules sandwiched between metal electrodes. The connection of molecular switching elements to the molecular wires that will be required for high-density integration and the function of such structures remains a substantial challenge.

Nanometer-diameter single-walled carbon nanotubes (SWNTs) exhibit unique electronic, mechanical, and chemical properties that make them attractive building blocks for molecular electronics (6, 7). Depending on diameter and helicity, SWNTs behave as one-dimensional metals or as semiconductors (8), which, by virtue of their great mechanical toughness and chemical inertness, represent ideal materials for creating reliable, high-density input/output (I/O) wire arrays. However, viable strategies for introducing molecular-scale device functionality into such I/O lines have not been established. SWNTs have been used to make low-temperature single-electron (9) and room temperature field effect (10) transistors. Smaller devices based on intratube junctions have been proposed (11) and observed recently in experiments (12), although no approaches yet exist for either the controlled synthesis of nanotube junctions or the integration of many addressable junctions as needed for molecular-scale computing.

Our concept for integrated molecular electronics differs substantially from previous efforts (2–5), because it exploits a suspended SWNT crossbar array for both I/O and switchable, bistable device elements with well-defined OFF and ON states (Fig. 1). This crossbar consists of a set of parallel SWNTs or nanowires on a substrate and a set of perpendicular SWNTs that are suspended on a periodic array of supports (Fig. 1A). Each cross point in this structure corresponds to a device element with a SWNT suspended above a perpendicular nanoscale wire. Qualitatively, bistability can be envisioned as arising from the interplay of the elastic energy, which produces a potential energy minimum at finite separation (when the upper nanotube is freely suspended), and the attractive van der Waals (vdW) energy, which creates a second energy minimum when the suspended SWNT is deflected into contact with the lower nanotube. These two minima correspond to well-defined OFF and ON states, respectively; that is, the separated upper-to-lower nanotube junction resistance will be very high, whereas the contact junction resistance will be orders of magnitude lower. A device element could be switched between these well-defined OFF and ON states by transiently charging the nanotubes to produce attractive or repulsive electrostatic forces. On the basis of this switching mode, we can characterize the elements as nano- or molecular-scale electromechanical devices.

In the integrated system, electrical contacts are made only at one end of each of the lower and upper sets of nanoscale wires in the crossbar array, and thus, many device elements can be addressed from a limited number of contacts (Fig. 1B). At each cross point (n, m) in the array, the suspended (upper) SWNT can exist in either the separated OFF state or the ON state in contact with the perpendicular nanotube on the substrate (lower SWNT). The ON/OFF information at an (n, m) element thus can be read easily by measuring the resistance of the junction and, moreover, can be switched between OFF and ON states by applying voltage pulses.
at electrodes $n$ and $m$. This approach suggests a highly integrated, fast, and macroscopically addressable nonvolatile random access memory (RAM) structure that could overcome the fundamental limitations of semiconductor RAM in size, speed, and cost.

To quantify the bistability and switching behavior of the proposed device element, we calculated the total energy $E_T$

$$E_T = E_{vdw} + E_{elas} + E_{elec} \tag{1}$$

where $E_{vdw}$ is the vdW energy, $E_{elas}$ is the elastic energy, and $E_{elec}$ is the electrostatic energy for the device. The first two terms in Eq. 1, which define the static potential, were evaluated to assess the range of parameters that yield bistable devices. The vdW interaction between nanotubes was calculated by pairwise summation of a Lennard-Jones potential that has been previously shown to provide good agreement with experiments for nanotube systems (13, 14). The elastic contribution to the total energy was determined with a beam mechanics model

$$E_{elas} = \frac{6(kB)^{1/4}}{\sqrt{2}(3 + 3bL + 3(\beta L)^2 + (\beta L)^3)}(8z)^2 \tag{2}$$

where $B$ is the product of the nanotube elastic modulus and geometric moment of inertia, $k$ is the elastic modulus of the support, $L$ is the length of the suspended nanotube, $\beta = 1/\sqrt{2} (k/B)^{1/4}$, and $8z$ is the displacement of the suspended tube from its unstrained position (15). Our calculations show that the proposed SWNT device structure will exhibit bistability for a broad range of parameters (Fig. 2). The 20-nm device in Fig. 2A exhibits ON and OFF states that are stable at room temperature (i.e., barrier $> 10k_B T$; $k_B$ is the Boltzmann constant and $T$ is temperature) for initial separations ranging from 1.0 to 2.2 nm. The calculated structures of the SWNT device element in the OFF and ON states for an initial separation of 2 nm (Fig. 2B) highlight the relatively minor distortion of the upper SWNT in the ON state (this nanotube does not buckle or kink when deformed), even when the initial separation is near the upper limit for bistability and deformation is at a maximum. These calculations also show that the potential is bistable for a wide range of device sizes when the upper nanotube is supported on either hard (Fig. 2C) or soft organic (Fig. 2D) materials. The minimum bistable device size for a hard support such as silicon is $< 10$ nm, and softer organic supports enable bistability for devices that are $< 5$ nm. Both types of materials could be envisioned for device fabrication.

There are several important points that can be drawn from these calculations. First, there is a wide range of parameters that yield a bistable potential for the proposed device configuration. The robustness of the ON/OFF states strongly suggests that this architecture will be tolerant of variations in structure that inevitably arise during fabrication by, for example, self-assembly. Second, the differences in separation between nanotubes in the ON and OFF states will produce large differences in resistance [i.e., $I \sim \exp(-kd)$, where $I$ is the current, $k$ is a decay constant on the order of $2 \text{ Å}^{-1}$, and $d$ is the tube-tube separation in angstroms] and thus should enable reliable reading of the ON and OFF states independent of variations in cross-contact resistance. Third, the range of mechanical strains required to achieve bistability in Fig. 2A, 0.22 to 1.7%, is well below the elastic limit of at least 6% [determined computationally (16) and experi-
checked carefully to see that it satisfied the condition. The calculated electrostatic potential was determined by the time to move the upper ends of the nanotubes, and thus, one interconnect can be used to address many individual junction elements. We also stress that each element can store a nonvolatile bit, whereas in current silicon-based devices a transistor and capacitor are required to store a bit in dynamic RAM or four to six transistors are required to store a bit in static RAM.

Second, the switching time for a 20-nm device, $10^{-11}$ s, suggests that ON/OFF switching operations can be carried out at 100 GHz (22). This switching time will decrease to $\approx 5 \times 10^{-12}$ s (200-GHz operation frequency) for a 5-nm element owing to the smaller effective mass, because the switching time is determined by the time to move the upper nanotube between its ON or OFF positions. The electrostatic charging time could also be important in device arrays made from SWNTs longer than 10 to 100 $\mu$m (22). Finally, we note that the nonvolatile nature of our devices is preferable from the standpoint of power consumption and corresponding heat dissipation as compared to dynamic RAM, which must be continually refreshed.

To determine whether this nanotube device concept can be realized, we have studied the properties of suspended, crossed nanotube devices made from SWNT ropes (23) by mechanical manipulation (Fig. 4). Current-voltage ($I$-$V$) measurements made on the lower and upper nanotubes of a typical model device show ohmic behavior with resistances of 11 and 58 kilohms, respectively (Fig. 4A). The $I$-$V$ curves between the upper and lower ropes in the OFF state were nonlinear, which is consistent with tunneling, with a resistance on the order of a gigohm. After switching ON, the $I$-$V$ curves exhibited ohmic behavior with a resistance of 112 kilohms (Fig. 4B). This large change in resistance is consistent with our predictions for OFF versus ON states in the suspended device architecture. Reversible switching between well-defined ON and OFF states has also been observed in several devices (Fig. 4C). The smaller change in ON/OFF resistances for the device in Fig. 4C is thought to arise from large contact resistances that are sometimes observed with nanotube ropes (24). Nevertheless, this change between ON and OFF states is 10-fold and persisted over several days of study. We think that these experiments represent clear proof of concept for our proposed architecture. Lastly, we have found that some of the devices fabricated from ropes could only be switched ON for reasonable applied voltages. This behavior is expected for potentials that have deep vdW minima (Fig. 2A). Irreversible switching could be exploited to configure logic elements for computing (3).

We think that our calculations and experimental results clearly demonstrate the potential of our nanotube-based device architecture. There are several issues that must be addressed in order to take the next steps toward integrated
molecular electronics. First, it is recognized that current SWNT samples consist of a random distribution of metallic (M) and semiconducting (S) tubes (8), and this might complicate device reading. However, the differences in resistance for M/M, S/S, and M/S SWNT cross-sections are much smaller than that between the ON and OFF states, and thus, these states will be robust even with a mixture of different tubes. Second, an inherent limitation of crossbar memory architectures, such as in Fig. 1, is the possibility of multiple electrical pathways (25). A standard solution to this problem is the incorporation of diodes at each cross point. This effective solution could be implemented in our system without the incorporation of additional elements by using semiconductor nanotubes or nanowires (7) for the lower molecular wires and metallic nanotubes for the upper SWNT because this would create a rectifying M/S junction at each cross point. Although it is not clear that it will be possible to exploit such an elegant solution with nanotubes until separated M and S SWNTs can be produced, the use of semiconductor nanowires for the lower wires could lead to rectification at each cross, independent of the type of suspended SWNT (26). Lastly, it will ultimately be important to create devices in parallel using individual SWNTs.

we think that this will be possible using either direct metal-catalyzed chemical vapor deposition (27) from patterned catalysts or directed assembly of nanotubes from solution (28). The developments in these growth and assembly areas suggest that highly integrated SWNT device arrays, which represent the next step in our plans for molecular electronics, may be soon realized.

References and Notes

1. The 1997 National Technology Roadmap for Semiconductors (SEMATECH, Austin, TX, 1997).
15. The elastic energy of a nanotube suspended on hard and soft supports has been evaluated using linear equation [Eq. 2] and nonlinear beam-bending models (K. Kim, E. Joselevich, T. Rucks, J. W. Hutchinson, C. M. Lieber, manuscript in preparation). Calculations using the nonlinear model agree to within 1% of those using a computationally less costly linear model [Eq. 2].
18. Our recent studies of nanotube tweezers (P. Kim and C. M. Lieber, Science 286, 2148 (1999)) show experimentally that nanotubes can behave as robust electromechanical devices. In this latter work, the free ends of nanotube bundles could be deflected repeatedly using electrostatic forces to grab submi-
19. The electrostatic energy of the system was evaluated by solving the Laplace equation for the suspended nanotube geometry (Fig. 1), including the dielectric support layer. The Laplace equation in a general 3D geometry was solved using Green’s theorem [J. D. Jackson, Classical Electrodynamics (Wiley, New York, ed. 2, 1974)]. Green’s theorem converts the Laplace equation into the form of an integral equation. It implies that if the potential and its normal derivative on the boundary are known, then the electrostatic potential over all 3D space can be determined.
22. The mechanical switching time, \( \tau _{\text{mech}} \), was calculated by reducing the problem to that of an effective particle moving along the potential energy surface. At the switching voltage [where there is no barrier], \( \tau _{\text{mech}} = \frac{d}{V_{\text{switching}}} \) \( \approx 10^5 \) times lower than the OFF resistance.
26. Semiconductor nanowires can be specifically doped p-type or n-type [Y. Cui, X. Duan, J. Hu, C. M. Lieber, J. Phys. Chem. B 104, 5213 (2000)]. If the lower wires in our architecture are made from n-type nanowires, then rectifying behavior will be observed at each cross element, irrespective of whether the upper SWNT is metallic or semiconductor. Metallic SWNTs would produce M-S junctions, whereas semiconductor SWNTs, which [as previous studies have shown] behave like p-type materials (12), would form rectifying p-n junctions.
30. We thank J. W. Hutchinson, P. Kim, and J. Huang for helpful discussion and E. J. Sánchez for help with figures. C.M.L. acknowledges support of this work by the Defense Advanced Research Projects Agency and the Office of Naval Research.