"Bucky Shuttle" Memory Device: Synthetic Approach and Molecular Dynamics Simulations

Young-Kyun Kwon,[1] David Tománek,[1] and Sumio Iijima[2]
[1]*Department of Physics and Astronomy, and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824-1116*
[2]*NEC Corporation, Fundamental Research Laboratories, 34 Miyukigaoka, Tsukuba, Ibaraki 3058501, Japan*
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Thermal treatment is reported to convert finely dispersed diamond powder to multiwall carbon nanocapsules containing fullerenes such as C_{60}. We investigate the internal dynamics of a related model system, consisting of a $K@C_{60}^{+}$ endohedral complex enclosed in a C_{480} nanocapsule. We show this to be a tunable two-level system, where transitions between the two states can be induced by applying an electric field between the C_{480} end caps, and discuss its potential application as a nonvolatile memory element. [S0031-9007(99)08484-7]

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Carbon nanotubes [1,2], consisting of seamless and atomically perfect graphitic cylinders a few nanometers in diameter, have been synthesized in bulk quantities [3,4]. The unusual combination of their molecular nature and micrometer-size length [5,6] gives rise to uncommon electronic properties of these systems. Electrical transport measurements for individual nanotubes indicate that these systems may behave as genuine quantum wires [7], nonlinear electronic elements [8], or transistors [9]. Potential use of nanotube-based two-level systems for permanent data storage, discussed here, would significantly extend their range of application.

Here, we present evidence that unusual multiwall nanotube structures, such as the "bucky shuttle" [10], self-assemble from elemental carbon under specific conditions. Our molecular dynamics simulations indicate that the bucky shuttle shows an unusual dynamical behavior that suggests its use as a nanometer-sized memory element. We show that a nanotube memory would combine high switching speed, high packing density, and stability with nonvolatility of the stored data.

The system described in this study was produced by thermally annealing diamond powder of an average diameter of 4–6 nm which was prepared by the detonation method (Cluster Diamond, Toron Company Ltd.). The powder was heated in a graphite crucible in inert argon atmosphere at 1800 °C for 1 hour. This treatment transforms the diamond powder into graphitic nanostructures presented in transmission electron microscope images shown in Fig. 1. A large portion of this material consists of multiwall capsules with few layers, the smallest structures being fullerenes with a diameter close to that of C_{60}. In several cases depicted in Fig. 1, the enclosed fullerenes may move rather freely inside the outer capsule, like a bucky shuttle.

An enlargement of one of such structures in Fig. 1 is displayed in Fig. 2(a). Figure 2(b) illustrates a corresponding model, consisting of a C_{60} encapsulated in a C_{480} capsule. The energetics of the $C_{60}@C_{480}$ system is shown in Fig. 2(c). The ends of the outer capsule are halves of the C_{240} fullerene, the optimum structures to hold a C_{60} molecule at an interwall distance of 3.4 Å. These end caps connect seamlessly to the cylindrical portion of the capsule, a 1.5 nm long segment of the $(10, 10)$ nanotube [3]. The interaction between the unmodified C_{60} molecule and the enclosing capsule is similar to that found in C_{60} crystals and nanotube bundles [3]; it is dominated by a van der Waals and a weak covalent interwall interaction that is proportional to the contact area between the constituents. An additional image charge interaction,

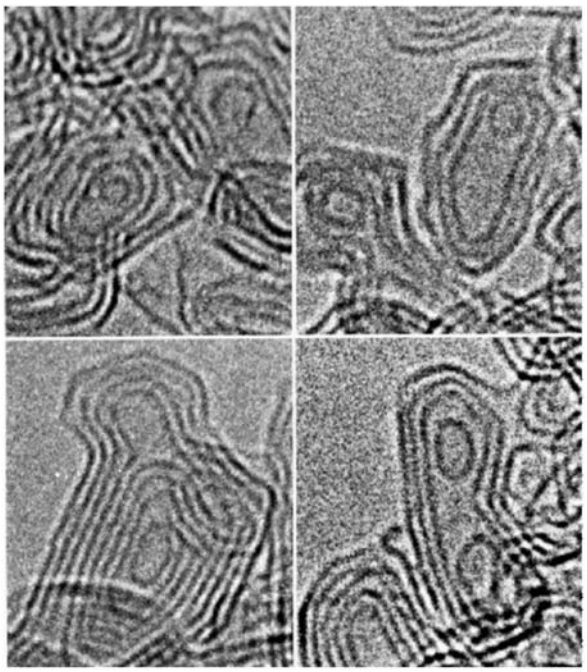

FIG. 1. Transmission electron microscope images depicting multiwall carbon structures that self-assemble during the thermal annealing of nanodiamond powder under the conditions described in this report. The smallest spherical structures are C_{60} molecules that are always found near the end of the capsule, where the attractive interwall interaction is strongest.

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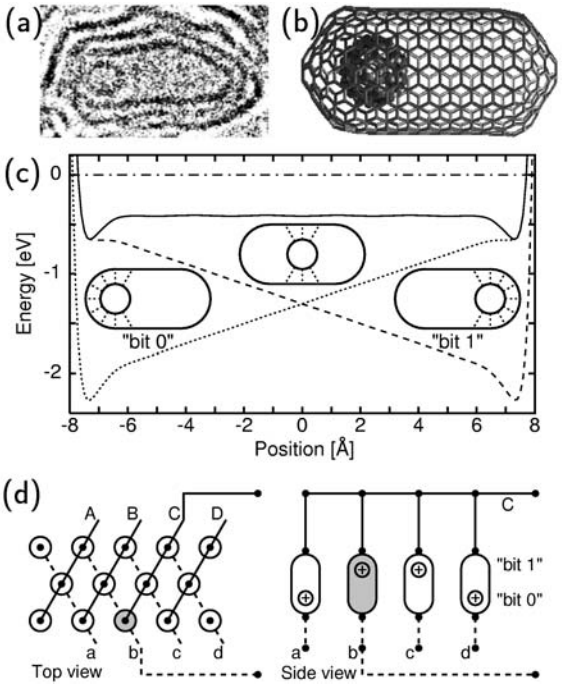

FIG. 2. (a) Enlargement of the upper-right section of the transmission electron microscope image in Fig. 1. (b) Structural model for an isolated $K@C_{60}^{+}@C_{480}$ bucky shuttle, with the $K@C_{60}^{+}$ ion in the "bit 0" position. (c) Potential energy of $K@C_{60}^{+}$ as a function of its position with respect to the outer capsule in zero field (solid line) and switching field $E_s = 0.1$ V/Å (dashed lines). The $K@C_{60}^{+}$ ion position, representing the information, can be changed by applying this switching field between the ends of the capsule. Energy zero corresponds to an isolated $K@C_{60}^{+}$ at infinite separation from the C_{480} capsule. (d) Schematic of a high-density memory board in the top and the side view. When a switching voltage is applied between conductors b and C, the corresponding bit information will be stored in the memory element bC at their intersection, shown shaded.

which is nearly independent of the C_{60} position, occurs if the C_{60} molecule carries a net positive charge, as we discuss below. Obviously, the van der Waals interaction stabilizes the C_{60} molecule at either end of the capsule, where the contact area is largest. This is reflected in the potential energy behavior in Fig. 2(c), and results in the likelihood of C_{60} being found near the ends of the capsule, as evidenced in Figs. 1 and 2(a). In the following, we will study the possibility of information storage in this two-level system.

Usefulness of this nanostructure for data storage implies the possibility to *write and read* information fast and reliably. Of equal importance is the capability to *address* the stored data efficiently, and the *nonvolatility* of the stored information.

In order to move the encapsulated C_{60} from one end of the capsule to the other (the molecular analog of writing) and to determine its position within the capsule (the molecular analog of reading) most efficiently, the C_{60} should carry a net charge. In the $K@C_{60}$ complex, which is known to form spontaneously under synthesis conditions in the presence of potassium, the valence electron of the encapsulated K atom is completely transferred to the C_{60} shell [11]. The C_{60} is likely to transfer the extra electron to the graphitic outer capsule, since the ionization potential of $K@C_{60}$ is smaller than the work function of graphite. The extra electron will likely be further transferred to the (graphitic) structure that holds this element in place. Since the enclosed K^{+} ion does not modify the chemical nature of C_{60}, we will model the dynamics of the $K@C_{60}^{+}$ ion in the neutral C_{480} capsule by uniformly distributing a static charge of $+1e$ over the C_{60} shell.

The *writing process* corresponds to switching the equilibrium position of the C_{60}^{+} ion between the "bit 0" and the "bit 1" ends of the capsule in an applied electric field. This is best achieved if the connecting electrodes, supplying the bias voltage, are integral parts of the end caps, to reduce the field screening by the nanotube [12]. The energetics of C_{60}^{+} in the switching field $E_s = \pm 0.1$ V/Å, generated by applying a voltage of ≈ 1.5 V between the end caps, is displayed in Fig. 2(c). One of the local minima becomes unstable above a critical field strength, causing the C_{60}^{+} ion to move to the only stable position. The switching field $E_s = 0.1$ V/Å is small and will have no effect on the integrity of the carbon bucky shuttle, since graphitic structures disintegrate only in fields $E \gtrsim 3$ V/Å [13,14].

The information, physically stored in the position of the C_{60}^{+} ion within the capsule, can be *read nondestructively* by detecting the polarity of the capsule. An alternative *destructive read* process would involve measuring the current pulse in the connecting wires, caused by the motion of the C_{60}^{+} ion due to an applied probing voltage. The total charge transfer associated with the current pulse, which is one electron in our case, may be increased by connecting several capsules in parallel to represent one bit, and by using higher charged complexes such as $La@C_{82}^{2+}$.

When targeting high storage densities, the *addressability* of the stored information becomes important. One possible way to realize a high-density memory board is presented in Fig. 2(d). Maximum density is achieved by packing the nanotube memory elements like eggs in a carton. Rows of nanocapsules can be connected at the top and at the bottom by nanowire electrodes in such a way that a single memory element is addressed at their crossing point. Applying a switching voltage between two crossing electrodes [e.g., the bC pair in Fig. 2(d)] will generate a nonzero field only in the memory element labeled bC. As in the ferrite matrix memory, many memory elements can be addressed in parallel using such an addressing scheme. This arrangement applies both for the writing and the destructive reading processes described above, and allows for multiple bits to be written and read in parallel. In the latter case, the status of the memory element bC is inspected by applying a switching voltage between the electrode pair b, C and monitoring the current in these electrodes.

Unlike in presently used dynamic random access memory (DRAM) elements, where information has to be sustained by an external power source, the *nonvolatility of the stored information* results from a nonzero trap potential near the "bit 0" or "bit 1" end of the capsule. Thermal stability and nonvolatility of data depend on the depth of this trap potential, which in turn can be adjusted by changing the encapsulated fullerene complex. The calculated trap potential depth of ≈ 0.24 eV for the $K@C_{60}^{+}$ ion near the ends of the capsule in zero field suggests that stored information should be stable well beyond room temperature and require temperatures $T \gtrsim 3000$ K to be destroyed. Further improvement of the thermal stability could be achieved using higher-charged endohedral complexes containing divalent or trivalent donor atoms, such as $La@C_{82}$ discussed above.

To study the efficiency of the writing process, we performed a molecular dynamics simulation of the switching process from "bit 0" to "bit 1" in the microcanonical ensemble of the $C_{60}^{+}@C_{480}$ memory element. We used a parametrized linear combination of atomic orbitals (LCAO) total energy functional [15], augmented by long-range van der Waals interactions [16]. Our computationally efficient $O(N)$ approach to determine the forces on individual atoms [17] had been previously used with success to describe the disintegration dynamics of fullerenes [18] and the growth of multiwall nanotubes [19]. A time step of 5×10^{-16} s and a fifth-order Runge-Kutta interpolation scheme was used to guarantee a total energy conservation of $\Delta E/E \lesssim 10^{-10}$ between successive time steps.

The results of our simulation are shown in Fig. 3. Initially, the C_{60}^{+} ion is equilibrated near the "bit 0" position. At time $t = 0$, a constant electric field of 0.1 V/Å is applied along the axis of the outer capsule. The originally stable "bit 0" configuration becomes unstable in the modified total energy surface, depicted in Fig. 2(c). The C_{60}^{+} ion is subject to a constant acceleration to the right, and reaches the "bit 1" position only 4 ps later, as seen in Fig. 3(a). During this switching process, the potential energy lost by the C_{60}^{+} ion is converted into kinetic energy, as seen in Fig. 3(b). Because of the small (albeit non-negligible) interaction between the encapsulated ion and the capsule, the kinetic energy gained initially occurs as rigid-body translational energy of the C_{60}^{+} ion. A nearly negligible energy transfer into the internal degrees of freedom due to atomic-scale friction, manifested in a very small increase of the vibrational temperature in Fig. 3(c), is observed during this initial stage of the switching process.

The C_{60}^{+} ion reaches the opposite end of the capsule, 4 ps after the switching field is applied, having gained 1.5 eV of net kinetic energy. This kinetic energy is too small to damage the capsule, as inelastic collisions involving C_{60} require energies exceeding 200 eV to occur [20]. Upon impact onto the enclosing capsule from the inside, a substantial fraction of this energy is converted into heat, thus increasing the vibrational temperature of the outer capsule by $\lesssim 10$ K and that of the C_{60}^{+} ion by ≈ 2 K. Because of the high heat conductivity and melting temperature $T_M \lesssim 4,000$ K of graphitic nanostructures [18], this modest heat evolution is unlikely to cause any structural damage even at high access rates.

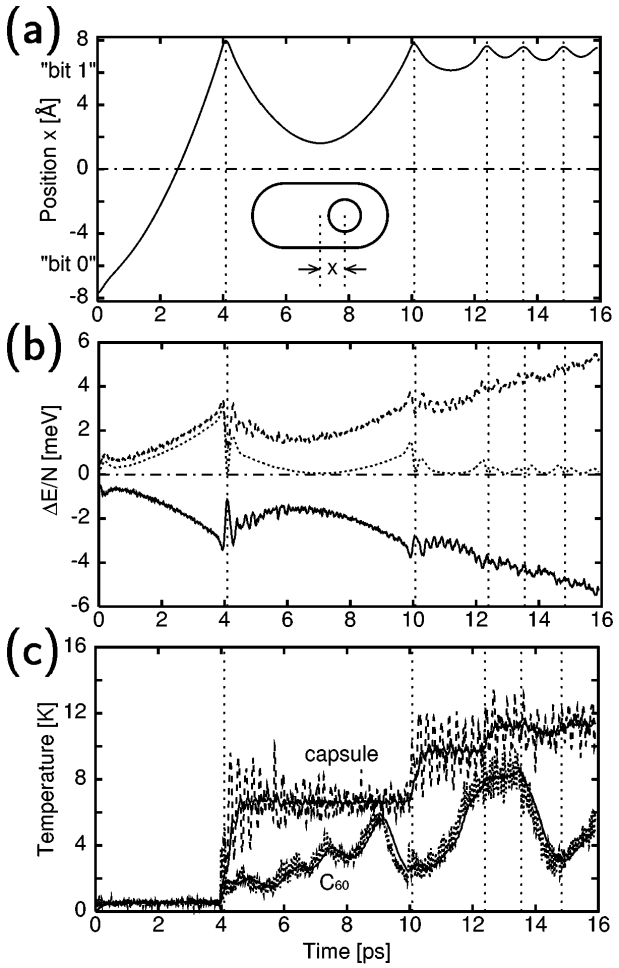

FIG. 3. Results of a molecular dynamics simulation of the switching process from "bit 0" to "bit 1", when a constant electric field of 0.1 V/Å is applied along the axis of the capsule. (a) Position of the $K@C_{60}^{+}$ ion with respect to the center of the enclosing C_{480} capsule as a function of time. (b) Changes in the potential energy (solid line) and kinetic energy (dashed line) in the laboratory reference frame as a function of time. The portion of the kinetic energy, corresponding to the translation of the enclosed $K@C_{60}^{+}$ ion with respect to the capsule (dotted line), is seen to decrease as the system temperature rises. The total energy (dash-dotted line) is conserved. All energies are given per atom. (c) Vibrational temperature of the enclosed $K@C_{60}^{+}$ ion (dotted line) and the enclosing capsule (dashed line) as a function of time. The solid lines are backward convolutions of the vibrational temperature values, using a Gaussian with a full-width at half maximum of 7.5×10^{-13} s.

As seen in Fig. 3(b), the net kinetic energy of the encapsulated C_{60}^{+} with respect to the outer capsule is significantly reduced during this collision. The C_{60}^{+} bounces back towards the middle of the capsule, slowed down by the opposing electric field, and finally turns again towards

the "bit 1" end. Figure 3(c) indicates that thermal equilibration in the system after the collision is achieved stepwise. The step period of ≈ 1 ps results from the beats between the low-frequency quadrupolar deformation modes of the colder encapsulated C_{60}^{+} ion and the hotter enclosing capsule, which have been excited during the quasielastic collision.

One or few oscillations of the C_{60}^{+} ion inside the enclosing capsule, damped by transferring energy from macroscopic to internal degrees of freedom, are necessary to stabilize it in the new equilibrium "bit 1" position, with a kinetic energy not exceeding the depth of the trap potential. As seen in Fig. 3(b), this situation occurs ≈ 10 ps after the initial onset of the switching field, thus resulting in an ideal memory switching and access rate close to 0.1 THz. In the slower sequential mode, this translates into a data throughput rate of 10 Gbyte/s, 4 orders of magnitude faster than the data throughput rate of 4–5 Mbyte/s which is achieved presently in magnetic mass storage devices.

In order to further reduce the switching time, one may consider increasing the field to shorten the transfer time between the two states, keeping in mind that the damping process would be prolonged in such a case. Unlike in our model simulation, there is no need to apply a constant switching field during the entire bit flip process. A 0.5 ps pulse of a 0.1–0.5 V/Å field is found to suffice to detach the C_{60}^{+} ion from its stable position and thus to change the memory state. This approach may be of particular use if an increase of the trap potential, due to a different fullerene complex, should be desirable.

Mass production of nanotube-based memory devices such as the one discussed here rely on the self-assembly of nanotubes and nanocapsules to ordered close-packed arrays. There has been encouraging evidence of such a self-assembly mechanism in the synthesis of free-standing nanotube ropes [3], aligned nanotube columns forming free-standing membranes [21], multiwall nanotube columns growing from a SiC(111) wafer [22], and most recently many C_{60} molecules inside long carbon nanotubes [23]. We also note that, since any double-wall nanocapsule with the enclosed structure shorter than the outer capsule behaves as a tunable two-level system, the functionality of the proposed nanoscale memory is basically independent of the exact size and shape of the encapsulated ion and the enclosing capsule.

In summary, we have shown that thermal treatment may convert finely dispersed diamond powder to multiwall carbon nanocapsules containing fullerenes such as C_{60}. Using molecular dynamics simulations, we investigated the internal dynamics of a related model system, consisting of a $K@C_{60}^{+}$ endohedral complex enclosed in a C_{480} nanocapsule. We showed this to be a tunable two-level system, where transitions between the two states can be induced by applying an electric field between the C_{480} end caps. This system, if considered as a memory element, would offer a combination of high switching speed, high density, nonvolatility of data, and relatively easy read/write access.

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