

Nonvolatile Memory Elements Based on the Intercalation of Organic Molecules Inside Carbon Nanotubes

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We propose a novel class of nonvolatile memory elements based on the modification of the transport properties of a conducting carbon nanotube by the presence of an encapsulated molecule. The guest molecule has two stable orientational positions relative to the nanotube that correspond to conducting and nonconducting states. The mechanism, governed by a local gating effect of the molecule on the electronic properties of the nanotube host, is studied using density functional theory. The mechanisms of reversible reading and writing of information are illustrated with a F_4 TCNQ molecule encapsulated inside a metallic carbon nanotube. Our results suggest that this new type of nonvolatile memory element is robust, fatigue-free, and can operate at room temperature.

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The concept of information as organized knowledge can be formally described, but dealing with practical information in the real world is generally related to a physical medium [1]. Operations on information such as processing, modification, and storage take place through processes based on intrinsic properties of matter, and from that point of view, it is the intricate interplay between information and physical mechanisms that constitutes the fundamental ground for information technology. Electronic switches can be considered as the fundamental basis for information processing and storage. In an electronic switch, the flow of electrons is modified by changing the state of the switching device, via a controlled writing mechanism, while the current flow through the device is used as a reading mechanism. Information is stored in the state of the switch, which can be modified either mechanically or electrically using the same or additional electrodes.

Any new technology that has the ambition to compete with conventional approaches must display significant benefits and distinct advantages. In that respect, carbon nanotubes are among the most cited candidate materials for nanoelectronics, a dominant position that stems mostly from their intrinsic structural and electronic properties [2]. The unique feature of carbon nanotubes that distinguishes them from other nanostructures, including conventional semiconductors and semiconductor nanowires, is their nearly perfect stoichiometry. While defects or dopant atoms in a semiconductor, or other imperfections such as a step edge, are not associated with significant changes in free energy, defects in nanotubes are related to changes in a covalently bonded pattern and thus are more difficult to form.

A number of devices based on carbon nanotubes have already been demonstrated in the laboratory, and some were shown to compete and even outperform their silicon analogs. For example, Derijcke *et al.* managed to selectively dope part of a single carbon nanotube placed over

three contacts and demonstrated the possibility of creating an intramolecular complementary carbon-nanotube field-effect transistor (CNFET) gate [3]. Using a similar type of CNFETs, Bachtold *et al.* realized an inverter [4]. It is possible to add a number of additional elements to these building blocks for basic nanocircuits, to obtain simple SRAM (static random access memory) elements, or NRAM (nanotube random access memory) such as the ones proposed by Kang *et al.* [5]. Use of air-stable ambipolar CNFETs in nanoscale nonvolatile memory cells operating at a few-electron level was reported by Radosavljevic *et al.* [6]. Novel memory concepts can also be developed by exploiting other carbon-nanotube architectures such as the crossbar arrangement of Rueckes *et al.* [7]. Further devices based on the functioning principle of electrically erasable programmable read only memory (EEPROM) by combining semiconducting and metallic carbon nanotubes have also been fabricated, for example with the realization of logical NAND gates by Fuhrer *et al.* [8]. Other speculative nanotube-based devices have also been proposed. For example, Kwon *et al.* proposed a device where a charged fullerene can be moved between the two ends of a nanotube at sites corresponding to ON and OFF states [9]. In most of these examples, the memory function is enabled by an additional element (e.g., nonvolatile gate or adhesive wall) that is extrinsic to the nanotube. Therefore, the stability and reproducibility of the storage device is controlled by the external component such as hard-to-control mobile surface charges or trap states in SiO_2 .

Here, we suggest a new type of carbon-nanotube memory device based on the modification of the transport properties of a conducting carbon nanotube that depend on the orientation of an intercalated functional molecule inside the nanotube host. The concept is based on the field effect induced by the presence of an acceptor molecule inside the tube. We used large-scale density functional

theory (DFT) calculations to simulate the operation of the new switching mechanism governed by quantum mechanical effects taking place at the nano- and molecular scales. This represents the ultimate scalability limit, which in a sense is similar to nonvolatile ferroelectric field-effect transistor and tunneling elements [1]. However, in this case, ferroelectric (or, rather, ferroelectroelastic, since the orientation states differ in electrostatic and strain energies) functionality is implemented at a single molecular level. The system can be switched between the ON and OFF positions, which correspond to stable orientations of the molecule. In addition to the reading mechanism, a writing mechanism that exploits the elastic properties of the nanotube is also demonstrated.

The electronic structure and energetics of molecular orientation were investigated using all electron density functional theory calculations using the NWCHEM package [10]. The Hamiltonian matrices were taken from converged calculations and used in the Green function formulation of Landauer-Buttiker theory to compute the quantum conductance [11]. Non self-consistent treatment of the transport is known to be accurate for small bias potentials as the ones used in this Letter [12]. Further details on the technique used for the present calculations are presented in Ref. [13]. Note that while the results shown here were obtained with local density approximation (LDA) for the exchange-correlation functional, no major difference was observed with other functionals, such as PBE0 [14].

The possibility of achieving large-scale air-stable and controlled doping was demonstrated recently with the encapsulation of organic molecules possessing different electron affinities and ionization energies inside of single-walled carbon nanotubes [13,15]. While a large variety of organic molecules can be used to dope carbon nanostructures, we focus here on the case of the *p*-doping tetrafluorotetracyano-*p*-quinodimethane (F_4TCNQ), since it is a molecule that has been shown to encapsulate fairly easily in carbon nanostructures [16]. During the course of our investigation, we discovered that most molecules possess a number of configurations relative to their host that correspond to stable or metastable geometries (Fig. 1(a)). We reported previously that the presence of an encapsulated molecule, in addition to being responsible for significant electron transfer onto or from the nanotube, does not modify drastically the quantum transport properties of the nanotube. This is confirmed for the stable perpendicular position (Fig. 1(b), dotted line) where we see that, close to the Fermi level, the transport properties are similar, though reduced by coherent scattering, to the ones of an unperturbed nanotube (Fig. 1(b), full curve). This is not the case when the molecule is parallel to the tube axis: in that case, the conductance is reduced dramatically (Fig. 1(b), dashed line). Since both positions correspond to local minima of the energy landscape, the system behaves precisely like a molecular switch: the system is in the conducting ON

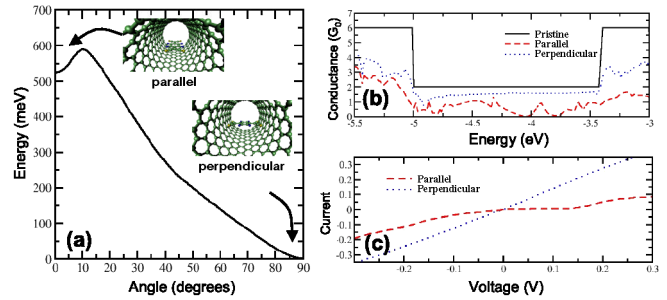


FIG. 1 (color online). (a) Total DFT energy of the F_4TCNQ molecule as a function of the angle between the main molecule axis and the nanotube axis. (b) and (c) conductance and current-voltage profile of three different open systems where the active region is seamlessly connected to semi-infinite (10,10) carbon nanotubes. Full, dashed, and dotted lines correspond to pristine case, parallel orientation, and perpendicular orientation, respectively.

position when the molecule is perpendicular to the axis and in the OFF position in the parallel configuration. This result cannot be understood from the assumption that the molecule only interacts weakly with the nanotube. The surprising result is that the conductance is altered the most when the molecule is the farthest away from the nanotube sidewalls. In the ON state, the F_4TCNQ 's terminal cyanide groups are as close as 2.8 Å from the tube sidewalls, while they remain relatively far away (~ 4.5 Å) in the parallel case.

A detailed understanding of the intrinsic electronic processes governing the switching mechanism is required in order to exploit its full potential. We now show that the switching mechanism presented above is based on general and fundamental concepts of molecular electronics. The task is to identify the force driving the two different behaviors shown in Fig. 1(b). For that reason, we examine the coupling between the electronic states of the molecules and those of the nanotubes. For that purpose, we have chosen a single F_4TCNQ molecule encapsulated in an $8 \times (10, 10)$ nanotube supercell as an active region that we repeated in a periodic fashion. The plane-wave DFT calculations presented in this Letter were performed using the VASP package [17]. Core atomic states were represented by projector augmented wave pseudopotentials [18] within the local density approximation for the exchange-correlation functional [19]. Plane-wave basis with an energy cutoff of 420 eV and a fine $8 \times 1 \times 1$ Monkhorst-Pack grid sampling of the one dimensional Brillouin zone were found to yield converged results [20,21]. The advantage of this approach is that the well-known electronic band-structure of the carbon nanotube can be easily identified. The DFT band-structures of the perpendicular and parallel configurations are shown in Figs. 2(a) and 2(d). Two important features can be seen. First, the Fermi energy of the pristine nanotube, located at the visible crossing of the π and π^* bands, is moved down by about 0.05 eV in each

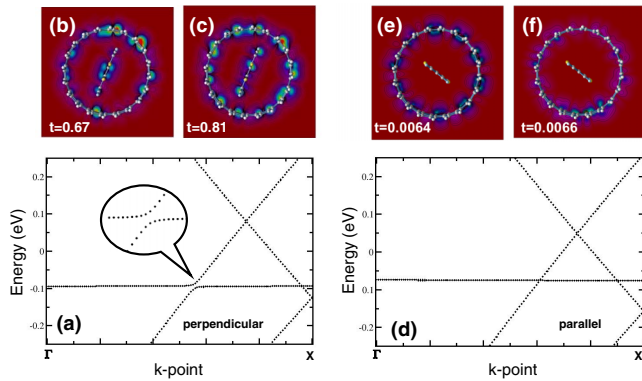


FIG. 2 (color online). DFT electronic band-structure of F_4TCNQ encapsulated inside a (10,10) carbon nanotube for the (a) perpendicular and (d) parallel configurations. The Fermi level is located at the origin of the Y -axis. (b) and (c) are 2-dimensional plots, in equatorial planes of the nanotubes, of scattered wave functions originating as Bloch states in the leads in the case of perpendicular orientation (there are two such states at the Fermi energy of the pristine tube). Individual transmission coefficients are given on the plot. Same plots for the parallel configurations are given in (e) and (f).

case, as expected for p -doping (i.e., electrons removed from the nanotube). Second, the F_4TCNQ molecular states couple weakly with the nanotube and manifest as straight undispersed lines located around -0.1 eV (the Fermi energy is positioned at the origin). Closer inspection of the band diagrams indicates that there is coupling and mixing with the nanotube's continuum of states, in the case of the perpendicular configuration (Fig. 2(a), inset). There is no such coupling in the OFF, parallel case.

This result seems *a priori* puzzling: the absence of coupling could mean that the properties of the host nanotube are not modified, and the resulting transport properties should therefore be similar to the ones of the unperturbed nanotube. Conversely, when the intercalated molecule modifies the nanotube properties, the molecular states could be seen as scattering centers responsible for degrading the transport properties of the assembly. This explanation would work without a correct alignment of the chemical potential of the active region and the ones of the semi-infinite leads due to charge transfer between the molecule and the nanotube. Here, it is the interplay between chemical potential shift and explicit coupling that governs the switching mechanism. In the OFF state, because the nanotube is positively charged, the bands are misaligned, and the incoming wave functions from the nanotube electrode cannot propagate through the active region. In the ON state, the modified electronic states no longer have the characteristics of the original bands, and the lack of alignment does not preclude transmission of electrons through the active region.

More insight into this can be obtained by examining the propagation of the individual Bloch states of the leads at the Fermi level. This information is obtained by building

the scattering matrix from the Green function of the open system using a procedure similar to the Fisher-Lee equation [22]. The resulting wave functions in the active region corresponding to the two Bloch states of the nanotube at the Fermi level are represented on Figs. 2(b), 2(c), 2(e), and 2(f). Using a transistor analogy, we note that the molecule effectively acts like a conventional field-effect gate: it blocks the electrons, but no electron actually scatters off it (no charge leakage). The only difference is that the gate is an intrinsic part of the device, and it is turned ON or OFF by displacing a single molecule. In the ON state, the molecular states are mixed with the nanotube's electronic structure, thereby allowing current flow, despite but also thanks to the large electron transfer between the molecule and the nanotube. The switching mechanism is therefore governed by a tunable “molecular gating” mechanism.

The molecular switching mechanism demonstrated can be complemented with a mechanism that allows for flipping between the two states of the system, i.e., for the controlled storage of information. Indeed, while “reading” the state of the system would consist in a measurement of the current flowing through the system at small bias potential, the “writing” part of the mechanism is not directly evident. There are a number of ways to modify the orientation of a molecule. For example, molecules with strong dipole moments will align with an applied static electric field. This is not possible for the type of systems we have presently since the electric field would vanish inside the metallic tube. Another attractive possibility would be to exploit the interaction of a molecular quadrupole moment and the large electric field gradient present in the vicinity of a metallic nanotube side-wall in the presence of an external field [23]. Here, we propose to make use of another remarkable property of carbon nanotubes subject to external deformation. While carbon nanotubes can undergo large axial deformations without breaking, they are also known to be very flexible [2]. Since the position of the encapsulated molecule in the switching device critically depends on the near-field interaction between the molecule and the nanotube atoms, small and controlled deformations of the nanotube should allow for reorientation of the molecule inside the tube.

We predict the molecule inside the tube can be flipped between parallel and perpendicular orientations by applying a radial compressive force on the tube. A plot of the energy (evaluated using the Tersoff-Brenner potential [24]) as a function of the deformation is shown in Fig. 3. Writing regimes can be distinguished by the amount of compression applied to the sidewalls: At small compression (~ 3 – 5%), the energy injected into the system is adequate to overcome the 80 meV barrier for parallel to perpendicular orientations. At larger compressions, the energy profile of Fig. 1(b) is severely modified, and the parallel orientation becomes more stable than the perpendicular one. For example, we verified using additional DFT calculations

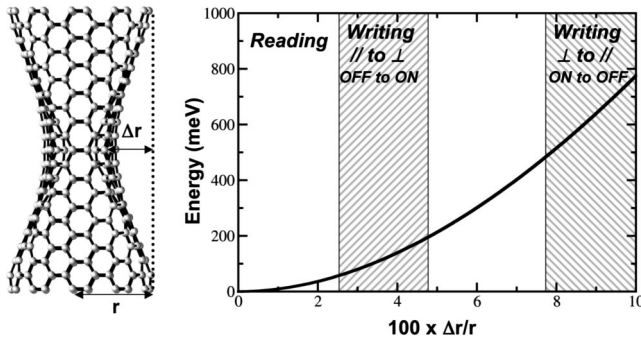


FIG. 3. Energy associated with radial compression of a (10,10) carbon nanotube. Three regimes can be identified: reading, OFF to ON (small deformation), and ON to OFF (larger deformation, up to 10%). Note that the compression of 50% illustrated on the ball-and-stick model is much larger than the functioning regimes of the memory element.

that at compressions of 10%, the perpendicular orientation becomes significantly less stable than the parallel one, and the energy barrier disappears. Since the nanotube is also a good thermal conductor, the additional energy quickly dissipates away from the active region after the change of orientation. The flipping mechanism does not alter the structure of the encapsulated molecule and involves deformation well below the plastic limit of the nanotube. Therefore, we expect the memory element to display low fatigue and large cyclability. The switching time is estimated to be in the picosecond range. In addition, the energy barrier for flipping (80 meV, see Fig. 1(a)) is higher than thermal energy at room temperature. The switching element is thereby promising as a nonvolatile memory, since it preserves the stored information without the addition of any energy.

We have proposed a novel nonvolatile memory element based on the interaction of an acceptor molecule encapsulated inside a metallic carbon nanotube. The fundamental requirement for the switching action is that the energy minima corresponding to the ON and OFF states should be nonequivalent, corresponding to stable and metastable states. Hence, realization of such a memory element requires (1) ensuring sufficient difference in electronic properties of the nanotube in both conformations as a basis for readout, (2) optimizing the potential energy landscape for the molecule to ensure the sufficient stability of both states, and (3) developing a practical reversible switching mechanism between the states. It follows that the new mechanism is not limited to the case of F_4TCNQ encapsulated in a given metallic nanotube. In fact, it could be applied, without much alteration, to any molecule-metallic nanotube system that displays the desired properties cited above.

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- [1] R. Waser, *Nanoelectronics and Information Technology: Advanced Electronic Materials and Novel Devices* (Wiley-VCH, Weinheim, 2003).
- [2] J. Bernholc, D. Brenner, M. Buongiorno Nardelli, V. Meunier, and C. Roland, *Annu. Rev. Mater. Res.* **32**, 347 (2002).
- [3] V. Derycke, R. Martel, J. Appenzeller, and P. Avouris, *Nano Lett.* **1**, 453 (2001).
- [4] A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekker, *Science* **294**, 1317 (2001).
- [5] J. Kang, J. H. Lee, H. J. Lee, and H. J. Hwang, *Physica E (Amsterdam)* **27**, 332 (2005).
- [6] M. Radosavljevic, M. Freitag, K. V. Thadani, and A. T. Johnson, *Nano Lett.* **2**, 761 (2002).
- [7] T. Rueckes, K. Kim, E. Joselevich, G. Y. Tseng, C. L. Cheung, and C. M. Lieber, *Science* **289**, 94 (2000).
- [8] M. S. Fuhrer, B. M. Kim, T. Durkop, and T. Brintlinger, *Nano Lett.* **2**, 755 (2002).
- [9] Y. K. Kwon, D. Tomanek, and S. Iijima, *Phys. Rev. Lett.* **82**, 1470 (1999).
- [10] R. A. Kendall *et al.*, *Comput. Phys. Commun.* **128**, 260 (2000).
- [11] S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, England, 1995).
- [12] W. Lu, V. Meunier, and J. Bernholc, *Phys. Rev. Lett.* **95**, 206805 (2005).
- [13] V. Meunier and B. G. Sumpter, *J. Chem. Phys.* **123**, 024705 (2005).
- [14] C. Adamo and V. Barone, *J. Chem. Phys.* **110**, 6158 (1999).
- [15] J. Lu *et al.*, *Phys. Rev. Lett.* **93**, 116804 (2004).
- [16] T. Takenobu *et al.*, *Nat. Mater.* **2**, 683 (2003).
- [17] G. Kresse and J. Furthmuller, *Phys. Rev. B* **54**, 11 169 (1996); *Comput. Mater. Sci.* **6**, 15 (1996); G. Kresse and J. Hafner, *Phys. Rev. B* **48**, 13 115 (1993).
- [18] P. E. Blochl, *Phys. Rev. B* **50**, 17953 (1994); G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [19] J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- [20] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [21] Given the distance between periodic images of the intercalated molecules, their direct interaction does not play an important role in the overall properties.
- [22] D. S. Fisher and P. A. Lee, *Phys. Rev. B* **23**, 6851 (1981); H. J. Choi, J. Ihm, S. G. Louie, and M. L. Cohen, *Phys. Rev. Lett.* **84**, 2917 (2000).
- [23] V. Meunier *et al.*, *Phys. Rev. Lett.* **93**, 246801 (2004).
- [24] D. W. Brenner, *Phys. Rev. B* **42**, 9458 (1990).