Molecular Dynamics Simulations of Nanomemory Element Based on Boron Nitride Nanotube-to-peapod Transition

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We investigated a nonvolatile nanomemory element based on boron nitride nanopeapods using molecular dynamics simulations. The studied system was composed of two boron-nitride nanotubes filled Cu electrodes and fully ionized endo-fullerenes. The two boron-nitride nanotubes were placed face to face and the endo-fullerenes came and went between the two boron-nitride nanotubes under alternatively applied force fields. Since the endo-fullerenes encapsulated in the boron-nitride nanotubes hardly escape from the boron-nitride nanotubes, the studied system can be considered to be a nonvolatile memory device. The minimum potential energies of the memory element were found near the fullerenes attached copper electrodes and the activation energy barrier was 3.579 eV. Several switching processes were investigated for external force fields using molecular dynamics simulations. The bit flips were achieved from the external force field of above 3.0 eV/ Å.

Keywords : Bucky shuttle memory device, Fullerene, Molecular dynamics simulation, Boron-nitride peapod, Boron-nitride nanotube, Nano nonvolatile memory

1. INTRODUCTION

The nanostructure and nanoparticles are of great interest in materials science and technology because of their interesting structures, especially their size. However, it is hard to control their physical and chemical properties. Fullerene-related materials have unique physical and chemical properties. Fullerene-related materials have attracted considerable attention due to their unique physical, chemical, optical, mechanical, magnetic, and electronic properties this last decade[1,2]. Compared to other nanostructures, fullerenes have found promising applications in a wide variety of very important technological processes such as in designing electronic devices, super-fibers, catalytic materials, etc[3]. Especially the large empty space (particularly inside carbon nanotubes (CNTs)) has opened also new applications as storage materials with high capacity and stability[4]. These cavities are large enough to accommodate a wide variety of atomic and molecular species, the presence of which can signify-cantly influence the properties of the materials. In particular, a new type of self-assembled hybrid structures called "nanopeapods", consisting of fullerene arrays inside single-walled CNTs, have recently been reported [5-10]. The application of nanopeapods ranges from nanometer-sized containers of chemical reactant[8] to data storage[11] and high temperature superconductor [12]. The encapsulation of fullerenes (such as C_{60}) in nanotubes is favorable on energetic grounds and occurs rapidly by exposing nanotubes to sublimed fullerenes. Mickelson et al.[13] reported how to pack C_{60} in boron nitride nanotubes(BNNTs). Moreover, Goldberg et al. [14] researched metal fillings inside BNNTs. Okada et al. [15] showed the reaction energy of a BN nanopeapod such as (10, 10)BNNT + C_{60}→ C_{60}@(10, 10)BNNT + 1.267 eV. Although the quantity of the exothermic energy, 1.267 eV, obtained from the calculations of Okada et al.[15] has been doubtful[16], C_{60}@(10, 10) BNNT is obviously more stable than the structure that the (10, 10) BNNT is infinitely separate with a C_{60} molecule. Kwon et al.[11] reported that multi-walled nanotubes called "bucky shuttle"[17] were synthesized from elemental carbon under specific conditions, and investigated bucky shuttle memory device, which acted as nanometer-sized memory element, using molecular dynamics (MD) simulations. In order to be applied as a device, the shuttle memory system is needed contacts or

electrodes and covered wires. Though CNTs are a representative nanostructure material, CNTs synthesized by experiments can be a semiconductor or a metal conductor by their chirality[2], because it is hard to control the chirality of CNTs. However, since most of bandgap of BNNTs are about 5.5 eV, they are electrically insulators[18].

For the bucky shuttle memory element suggested by Kwon et al.[11], the bit classifications must be very complicated to be defined and detected by the connected electrodes, because the shuttle media are always inside the same nanocapsule. For the bucky shuttle memory by Kwon et al., the stored data can be measured by the current pulse in the connecting wires, caused by the motion of the charged molecules due to the applied probing voltage. Therefore, to read the stored data, the $K^+@C_{60}$ should be shuttled. For example, when the $K^+@C_{60}$ settles in the position of 'bit 1', $K^+@C_{60}$ has to move toward the position of 'bit 0' during the data reading processes and then 'bit 1' can be measured. After the data reading, $K^+@C_{60}$ should be returned to the position of 'bit 1' to maintain its original data. Therefore, the data reading processes have to include the data erasing/writing processes, and then, both power consumption and data processing time increase. However, when $K^+@C_{60}$ comes and goes between separate nanocapsules, simpler data reading processing can be achieved. For the tube-to-peapod transition device proposed in this work, nonvolatility and data writing/erasing processes are the same as those for the bucky shuttle device by Kwon et al. However, for the data reading processes, our proposed system is different from that by Kwon et al., and this will be discussed in the next section.

If some processes, such as nanolithography, BNNT etching or cutting, C_{60} intercalation control, and the metal filling of electrodes, are used appropriately to fabricate aligned nanopeapods, the aligned bucky shuttle elements of separate nanocapsules can be synthesized. In this paper, we present the schematics of nanomemory devices based on the nanotube-to-nanopeapod transition. We expect that a memory element based on BN nanopeapods can be realized by nanotechnology based on nanosciences. Therefore, using classical MD simulations, we investigate the operations and the properties of a nanomemory element based on BN nanopeapods, in which data storage can be controlled by the transport of the ionized fullerenes using external force fields.

2. STRUCTURE AND METHODS

Many nanopeapods of endo-fullerenes have been investigated in experimental and theoretical studies. In this work, we assume that the charge of the endo metal encapsulated in fullerene is fully ionized such as F^-, Ne, Na^+, K^+, Mg^{2+}, and Al^{3+}[19]. In order to move the encapsulated endo-fullerenes, the endo-fullerenes should carry a net charge. Although there are many research results for the charge transfer and electron affinities of the endo-fullerenes[9], contrary results for the charge transfer the endo-fullerenes can have either a negative or a positive net charge. Therefore, we think that the charge transfer of endo-fullerene peapods should be investigated in further studies. In this work, we follow the assumption by Kwon et al.[11] for the charge of the endo-fullerenes encapsulated in BNNTs. Kwon et al. assumed that the C_{60} shell is likely to transfer the extra electron to the graphitic outer capsule. The extra electron on the outer capsule will likely be further transferred to the structure that holds the bucky shuttle device. Therefore, Kwon et al. modeled the dynamics of the $K^+@C_{60}$ ion in the neutral carbon capsule by uniformly distributing a static charge of +1e over the C_{60} shell. However, in our MD code, the endo metals were not included for computational efficiency, whereas the mass of C_{60} increased with the mass of the potassium atom and the charge of the C_{60} was assumed to be +1e and was uniformly distributed on the C_{60}, such as in the previous study by Kwon et al. Therefore, the charge per carbon atom was assumed to be +e/60.

The electronic properties of nanopeapods are very different from those of empty nanotubes[9]. Therefore, the changes of the electronic properties can make the definition or the classification of bits in the change of the current conduction. Therefore, if fullerene intercalation into BNNTs can be controlled by external force fields, the digit composed of 'bit 0' and 'bit 1' that is widely used in electronic memories devices can be considered in terms of the nanotube (as 'bit 0') and nanopeapod (as 'bit 1'). Micro-fluidic memory devices were recently demonstrated through the use of an aqueous viscoelastic polymer solution as a working fluid[20]. Under external force fields, since fully ionized $K@C_{60}^+$ can be accelerated, the $K@C_{60}^+$ can be shuttled by the alternative external force fields[11]. The bits of the proposed memory elements can be defined by the positions of the fullerenes. When the $K@C_{60}^+$'s come and go between separate nanotubes, the realization of a tube-to-peapod transition device is possible. Figure 1 shows schematics of the tube-to-peapod memory element proposed. The structure of the element for MD simulations in this study consists of two one-end-metal-filled (10, 10) BNNTs and three $K@C_{60}^+$'s. The open ends of the two (10, 10) BNNTs are face to face at an initial separation of 8 Å in the same tube axis, and then the structures are relaxed by the steepest descent (SD) method.

Therefore, the electronic properties of the two separate BNNTs can be controlled by the intercalation of the endo-fullerenes. If several technologies, such as nano-

scale electrode formation, metal filling, C_{60} intercalation control in BNNTs, the alignment of BN nanopeapods, nanolithography and BNNTs cutting can be supported, the following processes are suggested (a) copper filling in BNNTs, (b) C_{60} intercalation, (c) copper filling, (d) bridging between two electrodes using BN nanopeapods, (e) masking, (f) nanolithography, (g) etching, (h) endo-fullerene emission in one side BNNT using external force fields and evaporations, and (i) in order that the endo-fullerenes cannot escape from the system, the gaps between both BNNTs are reduced mechanically.

As shown in Fig. 1, the two electrodes that detect storage data are connected to BNNTs on the left-handside. When a bias (V_D) is applied between the two electrodes, the current tunneling of the empty nanotube is different from the current tunneling of the peapod. Therefore, semi-conducting nanotubes are more effective than metallic nanotubes for application in the memory device proposed. For the MD simulations in this study, we used (10, 10) BNNTs, since (10, 10) BNNTs are insulators [18]. While nonvolatility and data writing/ erasing pro-cesses are the same as those for the buck shuttle device by Kwon et al.[11], the data reading processes are different from those by Kwon et al.

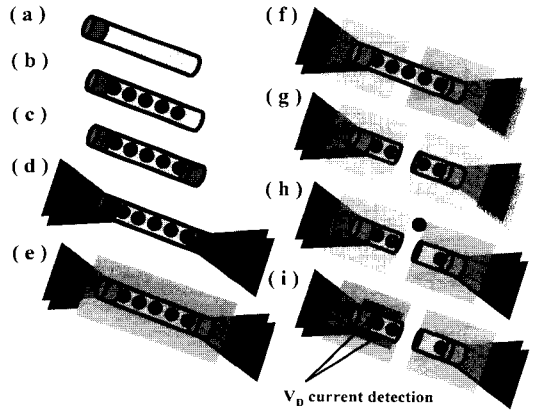

Fig. 1. Schematics of nanopeapod memory system proposed : (a) copper filling in BNNTs, (b) C_{60} intercalation, (c) copper filling, (d) bridging between two electrodes using BN nanopeapods, (e) masking, (f) nanolithography, (g) etching, (h) endo-fullerene emission in one-side BNNT using external force fields and evaporations, and (i) mechanical reduction of the gaps between both BNNTs.

For B–N interactions, we used the Tersoff-brenner potential function[21] that has been widely used. The long-range interactions were characterized with the Lennard-jones 12-6 (LJ12-6) potential. For BNNT wall and C_{60} interactions, we applied C_{60}–(10, 10) CNT interaction potential studied by Hodak and Girifalco[22], because we can not utilize parameters of the interaction between BNNT and C_{60}. For Cu-Cu interactions, used as the contacts, we used a LJ12-6 potential[23] with ε = 0.415 eV and σ = 2.277 Å. The structure of the copper electrodes was obtained from our previous work[24] that shows the copper nanowires encapsulated in armchair CNTs.

For carbon–carbon interactions, we used the Tersoff-brenner potential function[25] that has been widely applied to carbon systems. For copper-carbon interactions, we used a LJ12-6 potential[23] with ε = 0.0144 eV and σ = 2.040 Å. For Cu-BN interactions, we used the LJ12-6 potential with ε = 0.1448 eV and σ = 2.039 Å [23], because we cannot utilize parameters of the interaction between BNNT and Cu. For C_{60}- C_{60} interactions, we used a LJ 12-6 potential with ε = 0.00302 eV and σ = 3.47 Å[22].

We used both steepest descent (SD) and MD methods. The MD simulations used the same MD methods as were used in our previous works[24]. The MD code used the velocity Verlet algorithm, a Gunsteren-Berendsen thermostat to control temperature for all atoms. MD time step was 5×10^{-4} ps. We assume that the BNNTs interact with the substrate and the materials used as the mask still cover the BNNTs. Therefore, the atoms of the central BN ring along the tube axis are fixed during the MD simulations and the MD methods were applied to other atoms to avoid the shifts of the BNNTs due to the collisions between the fullerenes and the filled copper.

3. RESULTS AND DISCUSSION

Figure 2 shows binding energy as a function of the position of the central C_{60} fullerene. The central position of the C_{60} fullerene was initially 0 Å along the tube axis (z-axis). The length of the (10, 10) BNNT was 39.1 Å and 7 Å along the tube axis was filled with copper. After the system was fully relaxed by the SD method, the positions of the C_{60} were displaced by an increase of 0.1 Å and then the configurations were also relaxed by the SD method. The minimum potential energies are found near the fullerenes attached copper electrodes and the activation energy barrier is 3.579 eV. In our MD simulations, since the binding energy between a copper contact and a C_{60} is higher than that between C_{60} molecules, after the left and the right force fields were successively applied, active elements were always changed.

Two C_{60} molecules were always attached at the both end contacts and the shuttle medium was always the central C_{60} molecule. As shown in Fig. 2, the C_{60} always settles at both end copper filled of the BNNTs where the contact areas are large and the binding energies are high.

Therefore, in order for the fullerene to escape from the copper filled end of the BNNT, the fully ionized C_{60} molecule should be accelerated by applied force fields.

The operations of the studied memory element were investigated using classical MD simulations. Figure 3 shows the velocities (V_z), the position variation (P_z) of the shuttle fullerene along the tube axis as functions of MD step and external force field (F_{ext}). Temperature was 10 K in all cases. In Figs. 3(a) and (b), MD simulations have been performed for the different external force fields. External force field was initially 0 eV/Å until 200 steps; then the external force field was applied during 10,000 steps; and then, the external force field decreased zero state. The shuttle fullerene moved from the right side to the left side BNNTs. Peaks in the velocities (V_z) were found when the shuttle fullerene just before collided with the other fullerenes attached at both ends. After the collisions, the direction of the V_z were changed in the opposite directions. In Fig. 3(a), when the external force fields were -0.150 and -0.204 eV/Å, the shuttle fullerenes could not escape from the right side BNNTs. The shuttle fullerene was just accelerated to make rebound events. When the external force field was below -0.300 eV/Å, the bit flip in the system was not achieved. In Fig. 3(b), when the external force fields were -0.300 and -0.408 eV/Å, the shuttle fullerene were operated properly as a memory element. The filled circle symbol and the solid lines of Fig. 3(b) indicate the external force field of -0.300 and -0.408 eV/Å, respectively. The shuttle fullerene in the external force field of -0.408 eV/Å reached at the other side more faster than that in the external force field of -0.300 eV/Å.

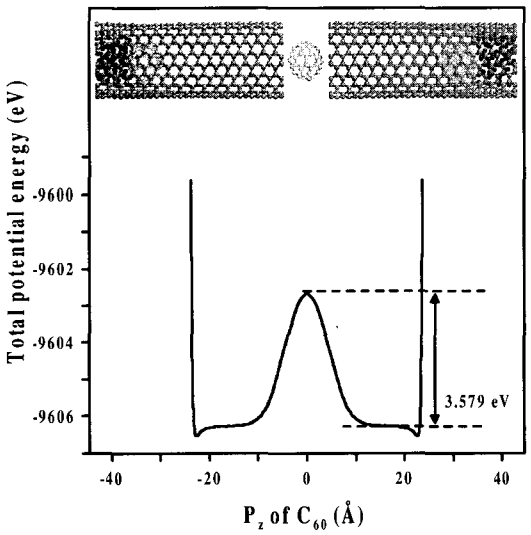

Fig. 2. Binding energy of the tube-to-peapod transition system as a function of the position of central C_{60} molecule.

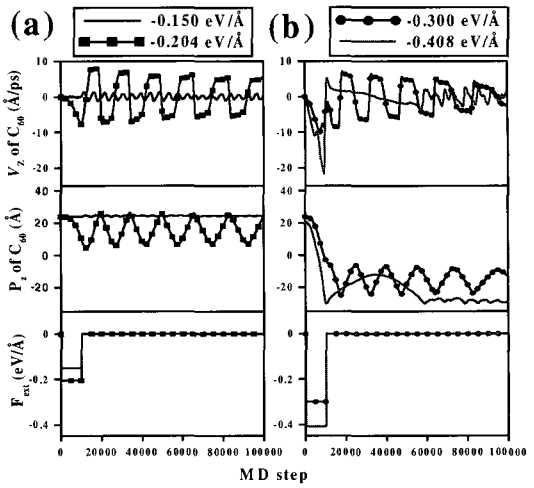

Fig. 3. Velocities (V_z) and the position variation (P_z) of the shuttle fullerene along the tube axis as functions of MD step and external force field (F_{ext}). MD temperature is 10 K. (a) The solid and the square symbol lines indicate the results of the external force field of -0.150 and -0.204 eV/Å, respectively. (b) The filled circle symbol and the solid lines indicate the results of the external force field of -0.300 and -0.408 eV/Å, respectively.

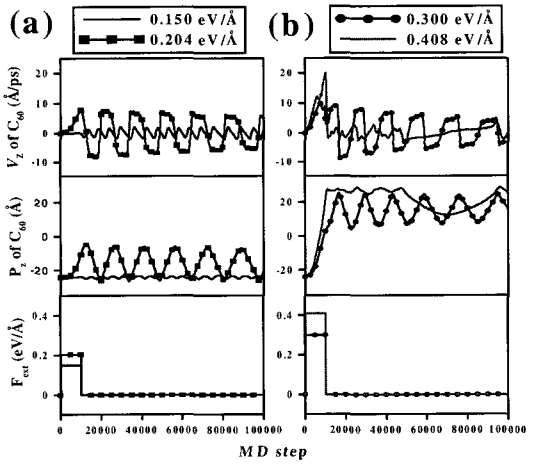

Fig. 4. Velocities (V_z) and the position variation (P_z) of the shuttle fullerene along the tube axis as functions of MD step and external force field (F_{ext}). MD temperature is 10 K. (a) The solid and square symbol lines indicate the results of the external force field of 0.150 and 0.204 eV/Å, respectively. (b) The filled circle symbol and the solid lines indicate the results of the external force field of 0.300 and 0.408 eV/Å, respectively.

Figure 4 shows the velocities (V_z) and the position variation (P_z) of the shuttle fullerene along the tube axis as functions of MD step and external force field (F_{ext}). Figure 4 was simulated in the same conditions in Fig. 3,

but the shuttle fullerene was started from the left side to the right BNNT. In Fig. 4(a), external force field was initially 0.2 eV/Å until 10,000 steps, and then decreased to 0 eV/Å. The shuttle fullerene was tried to move from the left side to the right BNNT. Peaks in the velocities (V_z) were found when the shuttle fullerene just before collided with the other fullerenes attached at both ends. After the collisions, the direction of the V_z is changed in the opposite directions.

The external force field made that the shuttle fullerenes collided between the fullerenes attached the end of copper electrodes in BNNT. In Fig. 4(b), when the external force field was over 0.300 eV/Å, the shuttle fullerene moved to the right side BNNT. The shuttle fullerene in the external force field of 0.408 eV/Å reached at the other side more faster than that in the external force field of 0.300 eV/Å.

Since the electronic properties of the BNNT can be changed by the fullerene encapsulations, the difference of current between BNNT and BN peapod can be detected. The bits can be classified by the current detection through the connected electrodes as shown in Fig. 1(i). So we can identify the memory status "0" or "1" by the difference of current between BNNT and BN peapod.

Since it is very difficult for the fullerene to naturally escape from the CNT, the proposed element can be applied to a nonvolatile memory device on the nanometer scale. Although the results obtained in this study are difficult to fully understand, our MD simulations showed that the fullerene shuttle memory elements based on the tube-to-peapod transition could be operated by the adequate external force fields. When several technologies are supported, we expect that the studied systems will be realized and used as an active device. This study shows the probability of a memory element occurring based on the boron nitride nanotube-to-peapod transition on the nanometer scale. To effectively operate the studied system, the switching speed, the applied force field, the active region, the length of the BNNTs, and the number of operating fullerenes should be considered in further studies.

4. SUMMARY

Using molecular dynamics simulations, we investigated the energetics and the operations of nonvolatile nanomemory elements based on boron nitride nanopeapods. The memory element studied in this paper was composed of two boron nitride nanotubes filled Cu electrodes and endo-fullerenes. The ends of the BNNTs were placed face to face at a separation of 8 Å, and the endo-fullerene shuttled between the two BNNTs under the alternatively applied force fields. In our idea, when the ionized endo-fullerenes are encapsulated in the BNNTs, the electronic properties of the boron nitride nanotubes are changed[9]. When the tube-to-peapod transition can be made by the adequate external force fields, the changes of their electronic properties can also be detected by tunneling current or conduction and then the bit classifications can be achieved. Since it has been well known that the fullerenes encapsulated in the nanotubes hardly escape from the BNNTs without external force fields, the studied system can operate a nonvolatile memory device. Since the interactions between the central fullerene and the copper electrodes of the end of the BNNTs stabilize the shuttle fullerene at both fullerenes attached to the copper electrodes where the binding energy was the largest, 3.579 eV, the external force fields should be applied under the conditions that the fullerene can escape from the copper electrode. Classical molecular dynamics simulations showed that the fullerene shuttle memory element based on the tube-to-peapod transition could be operated using an adequate external force field of above 3.00 eV/Å. The proposed system can also be applied to nano-electro-mechanical-systems as a nonvolatile memory device.

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