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Molecular memory with atomically smooth graphene contacts

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Abstract

We report the use of bilayer graphene as an atomically smooth contact for nanoscale devices. A two-terminal bucky-ball (C_{60}) based molecular memory is fabricated with bilayer graphene as a contact on the polycrystalline nickel electrode. Graphene provides an atomically smooth covering over an otherwise rough metal surface. The use of graphene additionally prohibits the electromigration of nickel into the C_{60} layer. The devices exhibit a low-resistance state in the first sweep cycle and irreversibly switch to a high-resistance state at 0.8 to 1.2 V bias. In the subsequent cycles, the devices retain the high-resistance state, thus making it write-once read-many memory.

Keywords: Graphene; Contact; Molecular memory; Write-once read-many; Bucky-ball

Background

Reliable and efficient contacts are an important aspect of device design at the nanoscale level. Historically, the contacts in the micron-scale devices have only been part of the overall device design for minimizing the contact resistance based on Schottky barrier height [1-3]. At the nanoscale level, however, the influence of contacts on the transport channel is so important that an equal or often times even more effort is spent on the contact and interface design [4,5]. In various nanoscale devices, the contacts even dominate the transport characteristics [6,7]. While various novel contacts exist at the nanoscale with unique density of states, the simplest ones are the ohmic contacts used to inject and extract the charge carriers. However, in addition to the atomic roughness and grain boundaries, such contacts suffer from electromigration or filament formation, which may deteriorate the device characteristics and lead to reliability issues [8]. One of the grand challenges thus for the nanoscale design is to provide smooth and reliable contact to nanomaterials, being free from electromigration and any other non-ideal effects. In this paper, our objective is to explore graphene [9,10] nanomembranes as a candidate for such contacts. The use of graphene and boron nitride has been explored earlier for ultrathin circuitry [11].

In this work, we report the use of bilayer graphene (BLG) as an atomically smooth contact in a molecular memory. Although various device structures based on graphene have been explored [12], our study is unique in the context of its use to improve reliability. BLG may prevent the electromigration of Ni atoms into the active material of the device. Furthermore, the use of BLG instead of monolayer or several-layer graphene is twofold. As compared to the monolayer, the probability of complete coverage with BLG is higher in the presence of defects. On the other hand, with the increasing number of layers, the transport properties of the device may be dominated by the multilayer graphene itself. Thus, BLG tends to provide an optimum trade-off.

Methods

The device schematic with BLG contact is shown in Figure 1a. We synthesized BLG on a 300 nm Ni film deposited on a 300-nm thermally grown oxide on Si substrate. Ni was deposited by using electron-beam evaporator (Angstrom Engineering, Kitchener, Ontario, Canada) at 1 Å/s rate under $< 7 \times 10^{-7}$ Torr chamber pressure. Ni pallets were placed in an alumina boat (both supplied by International Advanced Materials, Spring Valley, NY, USA) to avoid any contamination or residues. Prior to Ni evaporation, Si/SiO_2 substrate was cleaned with acetone for 10 min, methanol for 10 min, deionized (DI) water rinse for 10 min, then nanostrip for 20 min (commercial Piranha substitute), followed by DI water rinse for another 10 min.

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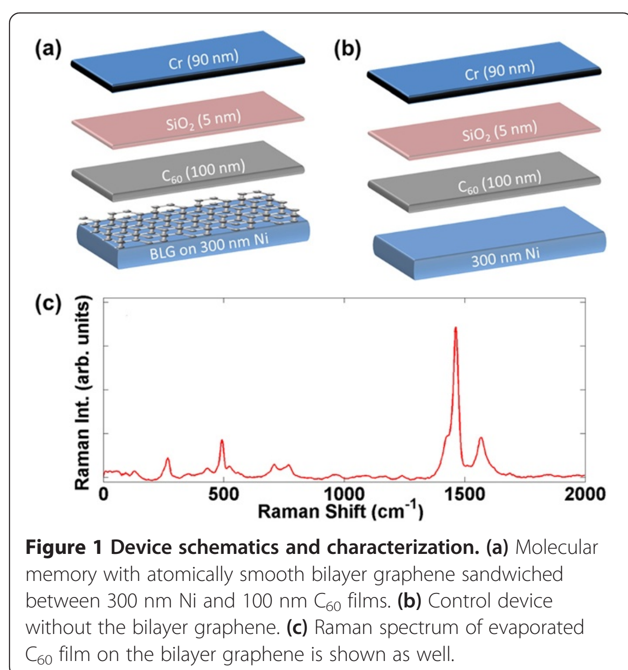

Figure 1 Device schematics and characterization. (a) Molecular memory with atomically smooth bilayer graphene sandwiched between 300 nm Ni and 100 nm C_{60} films. **(b)** Control device without the bilayer graphene. **(c)** Raman spectrum of evaporated C_{60} film on the bilayer graphene is shown as well.

This sequence removes the impurities from the SiO_2 surface and provides better Ni adhesion. After Ni evaporation, the sample was further processed in UV ozone cleaner (Novascan PDS-UV; Novascan Technologies, Inc., Ames, IA, USA) to remove any organic impurities on the Ni surface. The sample was then loaded into a homemade CVD furnace (Lindberg/Blue 1-in. diameter quartz tube; Thermo Fisher Scientific Inc., Waltham, MA, USA) at room temperature under Ar ambient with 200 standard cubic centimeter (sccm) flow rate. After ramping the temperature to 1,000°C, the sample was annealed in H_2:Ar (65, 200 sccm) ambient for 10 min. BLG was then synthesized by flowing CH_4:Ar (23, 200 sccm) for 2 min, and moving the hot portion of the tube to the room temperature by ultrafast cooling [13]. Research grade 5.0 (minimum purity 99.999%) process gasses supplied by Praxair Inc. (Danbury, CT, USA) were used. A 100 nm C_{60} film was deposited on the Ni/BLG structure, by using thermal evaporator (Edwards Coating System, E306A; Edwards Coating System, Sanborn, NY) at 1 Å/s rate under $< 7 \times 10^{-7}$ Torr chamber pressure. The commercial C_{60} powder was supplied by M.E.R Corporation (Tucson, AZ, USA). The use of C_{60} molecules ensures uniformity of the channel material constituents. Next, the sample was loaded in the electron-beam evaporator, and 5 nm of SiO_2 was evaporated, followed by 90 nm of Cr by using a shadow mask. The evaporation rates of SiO_2 and Cr were 0.2 and 1 Å/s, respectively, and the chamber pressure was $< 1 \times 10^{-7}$ Torr. A control sample without BLG was also fabricated as shown in Figure 1b. The thin layer of SiO_2 was used to protect C_{60} film during subsequent metal evaporation step.

A detailed characterization of the synthesized BLG has been reported earlier in [13]. Raman spectroscopy was used to confirm the quality of evaporated C_{60}. A laser power of 2 mW with 5 s scan time and four scans per point is used to avoid sample heating. The Raman spectrum of evaporated C_{60} film on BLG is also shown in Figure 1c. The dominant peaks are at 491, 1,464, and 1,596 cm^{-1} wavenumbers, which confirm the coherence of C_{60} molecular structure even after thermal evaporation [14,15].

Results and discussion

In Figure 2, we report the transport characteristics in the first and second sweep cycles for the device with BLG contact. The device starts in the low-resistance state and the voltage is increased in the forward direction until it irreversibly switches to high-resistance state at about 0.9 V, as shown in Figure 2a. After switching, the device withstands its high-resistance state, thus exhibiting hysteresis

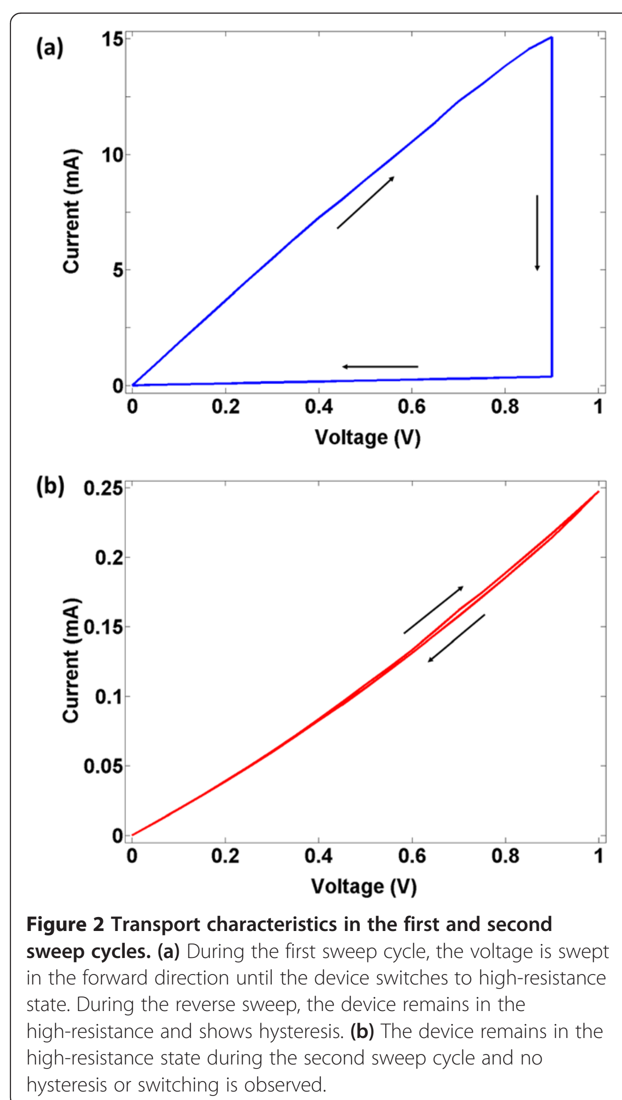

Figure 2 Transport characteristics in the first and second sweep cycles. (a) During the first sweep cycle, the voltage is swept in the forward direction until the device switches to high-resistance state. During the reverse sweep, the device remains in the high-resistance and shows hysteresis. **(b)** The device remains in the high-resistance state during the second sweep cycle and no hysteresis or switching is observed.

in the first cycle. We rule out the possibility of conductive filament formation (CFF) due to electromigration, since graphene has a breaking strength value of approximately 42 N/m and is impermeable even to helium atoms [16,17]. Moreover, in the CFF, current increases after switching, whereas an opposite trend is observed here. Apart from this, we find that the switching voltages for various devices lie in the 0.8 to 1.2 V bias range. This variation may be due to the amorphous and heterogeneous nature of the evaporated SiO_2 film [18].

The switching behavior for the second sweep cycle is shown in Figure 2b. The device remains in the high-resistance state without hysteresis. In the subsequent sweep cycles, the device sustains its high-resistance state, thus making it a write-once read-many (WORM) memory device.

Next, we report the retention characteristics in Figure 3, by using a read voltage pulse train of 0.4 V bias with 10 ms duration and 0.1% duty cycle. The mean value of current in the low-resistance state is 2.041 mA with a standard deviation of 0.973×10^{-3}. The device is then switched to the high-resistance state by applying a program voltage pulse of 1.2 V bias with 10 ms duration. The mean value of current is 89.29 μA with the standard deviation of 0.155. The current ratio of low-resistance to high-resistance state in this device is about 22.85 (which varied in 20 to 40 range for various devices). Besides the high retention time, the device also shows good endurance when continuous reading cycles with small pulse duration is applied. The retention characteristics are extrapolated to 10^4 s, and a stable behavior is foreseen in both states of the device.

For the control sample without the BLG contact, the device shows higher conduction with random switching, hysteresis, and significant variation from device to device.

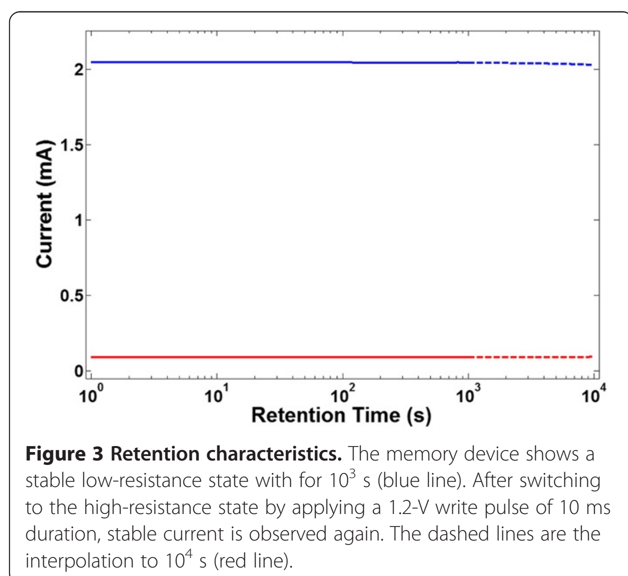

Figure 3 Retention characteristics. The memory device shows a stable low-resistance state with for 10^3 s (blue line). After switching to the high-resistance state by applying a 1.2-V write pulse of 10 ms duration, stable current is observed again. The dashed lines are the interpolation to 10^4 s (red line).

We attribute this irregular behavior in our control sample to the atomically rough interface between Ni and C_{60}, as well as the electromigration of Ni atoms across C_{60}/Ni interface.

The switching mechanism in the reported WORM memory device with the BLG contact is not clearly understood yet. However, we hypothesize that BLG prevents the electromigration of Ni atoms into C_{60} film, thus stabilizing the device behavior. The transport characteristics do not show ohmic or space-charge-limited conduction. Similar devices using C_{60} molecules have been reported to have rewritable switching characteristics - quite different from our observation [19,20]. Moreover, multilayer graphene electrodes used in devices with PI:PCBM composite as active material have also been recently reported to have WORM memory behavior, whereas with the metallic electrodes, rewritable switching characteristics have been reported [21]. Although the channel materials are different in the two experiments, the connection between the use of graphene and WORM features is noteworthy and needs to be explored further. Carbon nanotube-based contact [22] has also been explored to eliminate electromigration, however, we believe that graphene nanomembrane provides a better interface due to its 2D nature.

Conclusions

We have fabricated a molecular memory device with atomically smooth BLG contacts. Covering Ni film with BLG shields the channel from metal surface irregularities and also prevents the electromigration of Ni atoms into the C_{60} film. The device switches from a low-resistance to a high-resistance state, followed by hysteresis in the first sweep cycle. In the subsequent sweep cycles, the device remains in the high-resistance state and no hysteresis is observed, thus showing WORM memory behavior. The switching voltages vary in 0.8 to 1.2 V bias range for various devices with the high-resistance to low-resistance ratio in 20 to 40 range. The retention characteristics show good endurance under both low-resistance and high-resistance states up to 10^4 s. In addition, replacing the top Cr/SiO_2 contact with BLG may further improve the characteristics, which we leave for future work.

Competing interests

The authors declare that they do not have any competing interests.

Authors' contributions

AU, TR and HR have equal contribution to this work and the manuscript. All authors read and approved the final manuscript.

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