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Citation: *Appl. Phys. Lett.* **99**, 222109 (2011); doi: 10.1063/1.3663971

View online: <http://dx.doi.org/10.1063/1.3663971>

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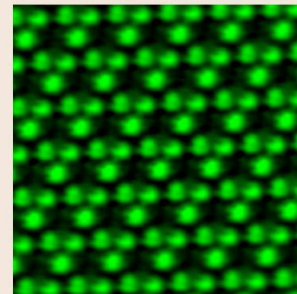
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Electronic interaction and bipolar resistive switching in copper oxide-multilayer graphene hybrid interface: Graphene as an oxygen ion storage and blocking layer

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(Received 24 September 2011; accepted 4 November 2011; published online 1 December 2011)

This study reports a bipolar resistive switching device based on copper oxide (CuO)-multilayer graphene (MLG) hybrid interface in complete contrast to the ohmic and rectifying characteristics of junctions based on individual MLG and CuO layers. The observed shift and the occurrence of additional O1s, Cu2p, and C1s core level peaks indicate electronic interaction at the hybrid interfacial layer. Large changes in the resistive switching parameters on changing the ambient conditions from air to vacuum establish the important role of MLG as oxygen ion storage and blocking layer towards the observed resistive switching effect. © 2011 American Institute of Physics. [doi:10.1063/1.3663971]

Hybrid devices involving two dissimilar materials having vastly different structural and electronic properties have been attracting much attention, because of the immense possibility of tailoring the device characteristics due to unique characteristics of hybrid interface.¹ Recent reports suggest that hybrid interfaces can be used to modify devices such as resistive memory device, lithium ion batteries, photovoltaic device, and light emitting devices.²⁻⁴ In addition, using organic and inorganic materials in bulk, thin film, or nanostructure forms, the devices having improved characteristics can be realized.⁵

In this Letter, bipolar resistive switching property of hybrid interface, between the inorganic CuO semiconductor and carbon based two dimensional structures, graphene, has been investigated. In the resistive switching phenomenon, memory cell undergoes reproducible resistance switching between two stable states named as high resistance state (HRS) and low resistance states (LRS).⁶ In this work, we report large modification in the electrical characteristics of CuO-MLG bilayer structure due to the electronic interaction at hybrid interface and oxygen intake capacity of multilayer graphene, resulting in reversible bipolar resistive switching properties.

Reduced graphene oxide was prepared by hydrazine reduction of graphene oxide prepared by modified Hummers method.⁷ Thereafter, it was ultrasonically dispersed in ethanol and then spin coated onto the copper base, resulting in deposition of multilayer graphene coating comprising of a stack of individual graphene sheets on Cu substrate. This layer will be referred to as multi layer graphene (MLG). A thin film of CuO was deposited over MLG layer using rf magnetron sputtering, followed by deposition of Ti top electrode over copper oxide, as reported earlier.⁵ I-V characteristics of Ti-CuO-MLG-Cu, Ti-CuO-Cu, and Ti-MLG-Cu have been studied using 2400 sourcemetre. X-ray photoelectron spectroscopy (XPS) was carried out using Perkin Elmer ultra high vacuum

XPS system (Model 1257), Minnesota, USA. The CuO-MLG sample for XPS studies were prepared by a thin layer of CuO (~10 nm) onto MLG, which were spin coated on silicon substrate. Depth profile analysis of CuO, MLG, and CuO-MLG samples was carried out using 4 keV Ar⁺ ions at a sputtering rate of 1 nm/min.

Individual CuO and MLG layers used for fabricating hybrid interface were characterized using glancing angle x-ray diffraction (GAXRD), x-ray photoelectron spectroscopy (XPS), and Raman spectroscopic techniques, showing phase purity of these layers (not shown here). Fig. 1(a) shows I-V curve during electroforming process performed on the pristine Ti-CuO-MLG-Cu sample. Electroforming occurs at a voltage (V_F) of -0.84 V. After this preliminary electroforming step, the Ti-CuO-MLG-Cu cell turns into LRS and exhibit linear I-V characteristics up to 0.47 V on the positive side as shown in Fig. 1(b) and switches from LRS to HRS at a reset voltage (V_R) of 0.48 V. On further increasing the voltage on the positive side, no transition from HRS to LRS is observed up to 0.84 V. As set voltage (V_S) is expected to be less than the V_F , it can be concluded no switching takes place from HRS to LRS on the positive voltage side. On sweeping the voltage towards negative side, the sample switches back from HRS to LRS at a set voltage (V_S) of -0.68 V. Observed set and reset transitions occurring at opposite polarity is indicative of bipolar resistive switching with typical resistance values in LRS and HRS to be ($\sim 58\Omega$) and ($\sim 64 \times 10^3\Omega$) at a read voltage of 0.1 V. The high value of resistance ratio ($\sim 1.1 \times 10^3$) between LRS and HRS is quite attractive from application point of view. Figure 1(c) shows the double logarithmic plot of the I-V curve for the positive and negative voltage regions showing ohmic behaviour with an approximate slope of 0.99 and 0.94 , respectively. However, the conduction behaviour in the HRS in both positive and negative voltage regime shows linear behaviour at lower voltage with slope increasing with increase of voltage, indicating multiple charge transport mechanism are responsible for resistive switching.⁸ Figure 1(d) shows the endurance characteristics of the Ti-CuO-MLG-Cu memory cell under ambient condition. It was

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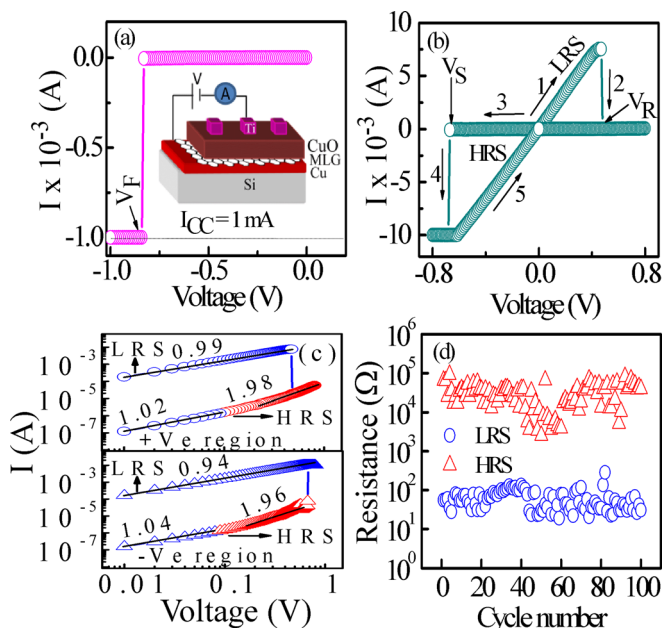


FIG. 1. (Color online) (a) Current-voltage characteristics of Ti-CuO-MLG-Cu sample during initial electroforming step showing transition to low resistance state (LRS) at forming voltage (V_F) of -0.84 V with a current compliance limit (I_{CC}) of 1 mA. Inset shows the schematic view of Ti-CuO-MLG-Cu structure. (b) I-V curve showing reversible and bipolar resistive switching in Ti-CuO-MLG-Cu sample under ambient condition. The sample switches from LRS to HRS at reset voltage (V_R) of 0.48 V and switches back to LRS at set voltage (V_S) of -0.68 V. The arrow indicates the sweep direction. (c) I-V characteristics showing the linear ohmic behavior with slope of about 0.99 and 0.94 in the LRS for the positive and negative bias region respectively in a double-logarithmic plot. Linearity is also observed in HRS at lower voltages with the slope of about 1.02 and 1.04 for both the regions. Deviation from the linearity is observed in HRS at higher voltages with the slope of about 1.98 and 1.96 for positive and negative regions respectively. (d) The endurance performance of the Ti-CuO-MLG-Cu based hybrid memory cell for about 100 cycles.

observed that well resolved two resistance states retain up to ~ 100 switching cycles without any serious degradation.

In contrast to the reversible bipolar switching observed in Ti-CuO-MLG-Cu sample, I-V curves for Ti-CuO-Cu structure at room temperature (300 K) and under ambient condition shows rectifying behaviour as shown in Fig. 2(a). Cupric oxide is a p-type semiconductor with a band gap of 1.2 eV and a work function of 5.32 eV. According to the Schottky model, a rectifying barrier is formed between a shallow work function metal ($Ti = 4.33$ eV) and a p type semiconductor ($CuO = 5.32$ eV).⁹ Graphene (4.5 eV) with its p-type nature is expected to form a low Schottky barrier with Ti and is consistent with the observed linear I-V curve for Ti-MLG-Cu structure with slope indicating a resistance value of 350Ω shown in Fig. 2(b). Large difference in the I-V characteristics and the absence of resistive switching behaviour in devices made from individual CuO and MLG w.r.t that of CuO-MLG based hybrid interface point towards a strong structural or electronic modification at the hybrid interface.

To study the nature of the CuO-MLG hybrid interface, XPS depth profile analysis giving the intensity of peaks at different depth of CuO-MLG sample was carried out (not shown here) and the results showed that the depth at about 12 min of sputtering corresponds to the interfacial region in the CuO-MLG structure. Figure 3(a) shows the C1s spectra of CuO-MLG and MLG sample after 12 min of sputtering. It

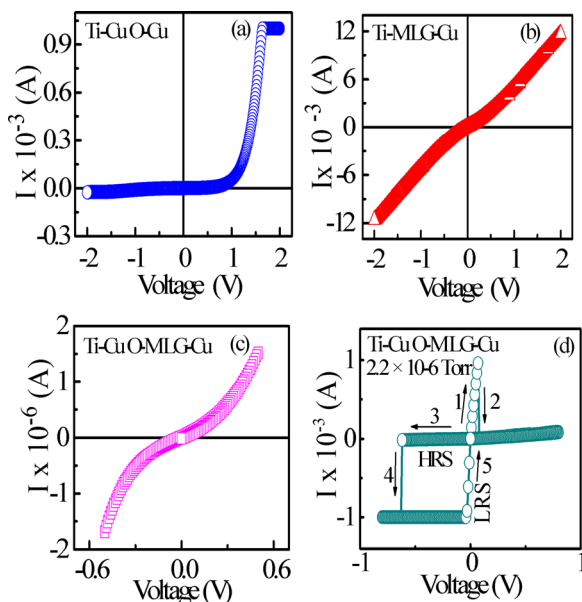


FIG. 2. (Color online) I-V curve showing (a) the rectifying characteristics for Ti-CuO-Cu, (b) nearly linear behavior for Ti-MLG-Cu, and (c) non linear characteristics before electroforming for Ti-CuO-MLG-Cu junctions. (d) I-V curve showing reversible bipolar switching for Ti-CuO-MLG-Cu sample under 2.2×10^{-6} Torr vacuum. The sample switches from LRS to HRS at reset voltage (V_R) of 0.07 V and switches back to LRS at set voltage (V_S) of -0.63 V.

was observed that the main C1s peak is observed at 284.5 eV in both the samples. An additional peak towards higher binding energy at 288.1 eV is observed in case of CuO-MLG sample. In Fig. 3(b), O1s spectra for CuO show two peaks; the main peak at binding energy of 530.0 eV corresponds to the oxygen of the CuO crystal lattice along with an appreciable shoulder at 531.8 eV in the O1s spectra corresponding to an additional oxygen species in the cupric oxide sample.¹⁰ MLG sample shows O1s peak at 531.6 eV, which is related to oxygen containing functional groups present due to hydrazine reduction step during synthesis of graphene. In the O1s spectra for the CuO-MLG interface, two peaks at 530.0 eV and 531.6 eV were observed corresponding to the lattice oxygen of CuO and due to oxygen from MLG, respectively, with the third peak due to “non-lattice” oxygen showing a 0.3 eV shift towards higher binding energy side w.r.t that observed in CuO sample. In Fig. 3(c), the Cu 2p spectra for CuO shows single peak at 932.6 eV, whereas for CuO-MLG sample, two peaks were observed at 932.3 and 934.2 eV. The additional peak at higher binding energy side in the Cu and C core level spectra for CuO-MLG sample shows the formation of copper carbide at the interface.¹¹ The shift in the O1s peak indicates interfacial interaction probably between the carbon from the graphene and oxygen species of CuO at the interface. This type of interfacial interaction has also been recently observed across the hybrid interface based on CuO-hexa-*peri*-hexabenzocoronene structure.⁵

The electroforming of the CuO-MLG hybrid interface can be explained by the electric field induced generation and migration of O^{2-} ions from CuO to graphene layer. As negative bias is applied on the Ti top electrode, CuO reduces into the Cu_2O or Cu which results in the generation of metallic copper and the oxygen ions. The generated oxygen ions migrate towards the graphene where it possibly interacts with

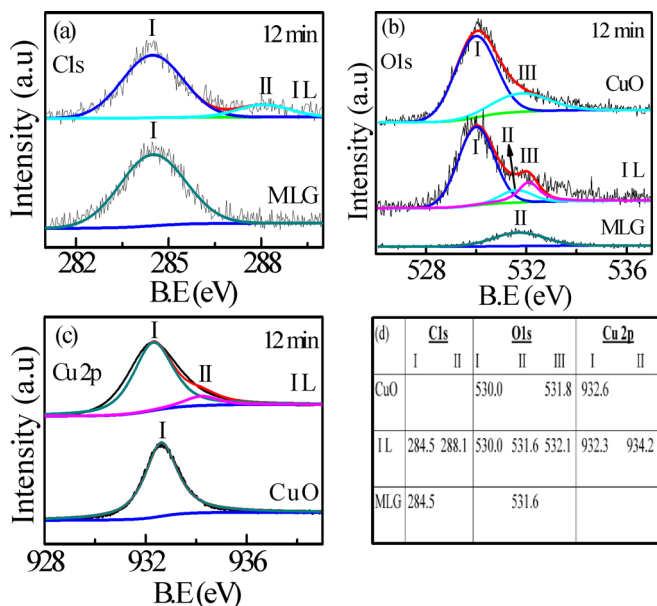


FIG. 3. (Color online) (a) XPS C1s spectra in CuO-MLG and MLG samples after sputter time of 12 min. Additional C1s peak at higher energy is observed for CuO-MLG interfacial layer (IL). (b) O1s spectra showing two peaks in CuO and CuO-MLG sample correspond to the lattice oxygen and “non lattice” oxygen of CuO, and an additional peak for CuO-MLG interface is due to the oxygen species in MLG layer. (c) The Cu 2p spectra for CuO sample shows a single peak, whereas CuO-MLG sample shows two peaks, one correspond to the cupric phase and other corresponds to the formation of copper carbide at the interface. (d) Tabulated results for peak positions in C1s, O1s, and Cu2p spectra for CuO, MLG, and CuO-MLG interface.

the various epoxide and carboxyl groups attached to the graphene layer. The metallic copper align themselves between the top Ti contact and CuO-graphene interface and the sample switches to LRS due to the formation of filamentary paths. The O^{2-} ion act as p type dopant, reducing resistance of the graphene layer and further reducing the resistance of LRS. It may be noted that the resistance of the hybrid structure in LRS is ($\sim 56\Omega$) smaller than that of multi layer graphene stack ($\sim 350\Omega$). On sweeping the voltage towards the positive side, the O^{2-} ions from the MLG migrate back towards the CuO layer and change the electrical properties of hybrid interface and transition from LRS to HRS takes place. As shown in Figs. 2(a) and 2(b), no resistive switching was observed in Ti-CuO-Cu and Ti-MLG-Cu samples. This confirms that the presence of graphene is important for electroforming and reversible switching. It is proposed that graphene also acts as a blocking layer and prevents the diffusion-out of oxygen gas from CuO film to the bottom electrode. Similar improvement due to blocking layer effect is also reported in Pt-Cu₂O-Pt stacked structure.¹²

To further understand the role of MLG layer on the resistive switching properties, I-V characteristic was studied under vacuum condition (2×10^{-6} Torr) and a large change in the switching parameters was observed in comparison to those observed in ambient condition. Reset current decreases from 10 mA to 1 mA and the reset voltage decreases from 0.48 V to 0.07 V on going from ambient to vacuum condition as shown in Fig. 2(d). In ambient conditions, the effect of

O^{2-} ion migration to the graphene layer gets neutralized as some of the oxygen species can combine with hydrogen or other ionic species present in MLG. It is expected that in vacuum conditions, the chemical dopant such as hydrogen ions (H^+) in the graphene layer are partially removed. Thus, relatively larger concentration of O^{2-} ions are available in MLG which can migrate to and from the CuO layer and thus lower value of electric field is required for migration of O^{2-} species to CuO layer. This explains lower value of reset voltage under vacuum conditions. The process of change over from HRS to LRS takes place due to migration of O^{2-} species from CuO layer to MLG, and hence set voltage is relatively unaffected under ambient or vacuum conditions. Similar reduction in behaviour of the I-V curves hysteresis has been reported in Au-graphene sample under vacuum in comparison to ambient due to the reduction of oxygen species.¹³

In conclusion, the observed reversible bipolar resistive switching in CuO-MLG sample is related to the formation of hybrid interfacial layer and reversible oxygen intake property of graphene layer. The shift in the O1s spectra and the occurrence of additional peaks in C and Cu spectra confirms the electronic interaction at CuO-MLG hybrid interface. Reduction in reset voltage and reset current on changing the ambient from air to vacuum confirms the role of graphene layers as reservoir of oxygen species. Back and forth transfer of O^{2-} species from MLG to CuO causes reversible changes in the electrical properties of CuO-MLG sample during bipolar switching. Multiple electron transport mechanism responsible for current transport also indicates that CuO, MLG, and interfacial layer together determine the electrical properties of the device, especially in HRS. In LRS, electrical resistance of the device is mostly due to the oxygen doped MLG layer as CuO and interface layer are electrically shortened due to the formation of metallic filamentary paths. This study presents an interesting application of graphene layer for improving the switching properties of resistive memory device.

One of the authors Bharti Singh is thankful to Council of Scientific and Industrial Research, India.

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