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Temperature-sensitive asymmetrical bipolar resistive switches of polymer:nanoparticle memory devices

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ABSTRACT

The interface between two bulk electronic materials can significantly affect the electrical behavior of electronic devices. But the interface between a bulk metal and metal nanoparticles has been rarely explored. This paper reports significant temperature effect on the asymmetrical resistive switches of polymer:nanoparticle memory devices. The devices have architecture of a polystyrene layer admixed with gold nanoparticles capped with conjugated 2-naphthalenethiol sandwiched between Au and Al electrodes. The devices exhibit significant resistive switches at room temperature. However, the resistive switches become less significant at temperature below 200 K, and they are not noticeable at 103 K. The temperature effect suggests that the resistive switches are assisted by the thermal energy. The charge transport through the devices has different mechanisms at high and low temperatures. At temperature above 220 K, the Poole–Frenkel emission is an important mechanism for the charge transport. At temperature below 220 K, the temperature-independent Fowler–Nordheim tunneling becomes an important process.

1. Introduction

Metal and semiconductor nanoparticles (NPs) have been attracting strong attention owing to their interesting electronic structure and unique properties related to their nanometer size [1–3]. For example, metal and semiconductor NPs can be charged like molecules. The Coulomb energy (E_c) to charge a nanoparticle can lead to interesting temperature effect on the charge transport through NPs [4–10]. When the thermal energy is higher or comparable to E_c, the charge transport through metal NPs can be a thermally activated process or even metallic behavior. When the thermal energy is lower than E_c, the charge transport becomes charge tunneling because of the Coulombic blockade. Many important applications have been reported for metal and semiconductor NPs. For example, they can be used as the active materials in electronic devices, including light-emitting diodes [11,12], photodetectors [13], solar cells [14,15], memory devices [16–18], and thermoelectric devices [19,20]. Resistive switches have been reported for devices with a polymer film admixed with metal NPs sandwiched between two conductive electrodes [16,21–34]. These polymer:nanoparticle devices can be switched between the two states with high and low resistances for numerous times, and thus they are promising to be the next-generation nonvolatile memory devices. The resistive switches are strongly affected by the capping ligand on the Au NPs, as the resistive switching mechanism is related to the charging and de-charging of the Au NPs [16,32–36]. When Au NPs capped with saturated organic ligands are used in the devices, the resistive switches are reversible and insensitive to the electrode. When Au NPs capped with conjugated organic ligands are used as the active material sandwiched between two Al electrode, the pristine device is in the high resistance state and it can be switched to a low resistance state. But the device cannot be switched back to the high resistance state.

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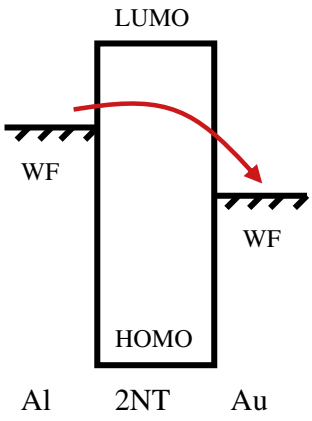
Although early polymer:nanoparticle memory devices have resistive switches insensitive to the electrodes, because metal nanoparticles capped with saturated organic ligands or oxides are used in these devices [16,37,38]. Electrode-sensitive resistive switches were observed on polymer:nanoparticle memory devices when a polymer layer admixed with Au NPs capped with conjugated organic ligands was used as the active layer between two electrodes of different work functions [39–41]. The electrode-sensitive switches are attributed to the charge transfer between the bulk Al electrode and the Au NPs in the active layer as a result of the different work functions of the Al electrode and the Au NPs. Scheme 1 shows the interface between a bulk Al electrode and Au NPs capped with conjugated 2-naphthalenethiol (2NT). Electrons can transfer from the Al electrode through 2NT into the core of Au NPs, as the work function of Al (4.1 eV) is higher than that of Au (5.1 eV). This interface is significantly different from that between two bulk metals or between a bulk metal and a bulk semiconductor [42]. When two bulk metals of different work functions are put in contact, there will be electron transfer from the metal of low work function into the metal of high work function. The electron transfer leads to a contact potential at the metal–metal interface. The contact potential does not affect the charge transport along the two polarities because the interface between two bulk metals is quite thin. Charge transfer also takes place for a Schottky junction formed by a bulk metal and a bulk semiconductor, which leads to the formation of a depletion region and a built-in potential at the interface. The charge transport through Schottky junction is quite asymmetrical because of the energy barrier at the interface, and the forward current is a thermally activated process. Different from the metal–metal and metal–semiconductor contacts, the metal–metal NP contact can give rise to asymmetrical resistive switches along the two polarities [39–41].

The resistive switches depends on the materials used for the devices [39,41]. As the resistive switches are related to the electron transfer between a metal electrode and Au NPs. The organic ligands on the Au NPs construct an energy barrier for the electron transfer. Their electronic structure thus significantly affect the resistive switches. The devices with Au NPs capped with benzenethiol exhibit higher current density for the devices in the low resistance state but lower threshold voltages (V_{th}) for the resistive switches than those with Au NPs capped with 2NT. On the other hand, when Au NPs capped with partially conjugated 2-benzeneethanethiol are used, the V_{th} values become very high whereas the current density for the devices in the low resistance state is very low. The electron transfer is due to the different work functions of a metal electrode and the core of the Au nanoparticles. When the Au electrode of a device with a structure of Al/Au NPs/Au is replaced with a metal of lower work function like Cu or Al, the V_{th} values become higher while the current density for the devices in the low resistance state becomes lower. The mechanism of the resistive switches arising from the electron transfer between a metal electrode and Au NPs is evidences by not only the electrode effect on the resistive switches but also the ac impedance spectroscopy of the devices in different resistance states [34]. The electronic behavior of the devices also depends on the thickness of the active layer and the loading of Au NPs [40]. The V_{th} values slightly increase when the active layer is thicker or the loading of the Au NPs in the active layer is lower. But the electronic behavior of the devices is insensitive to the polymer matrix. Because temperature strongly affects the electronic behavior for electronic devices exploiting the interfaces like Schottky and *p–n* diodes, it is expected that the temperature should significantly affect the resistive switches of polymer:nanoparticles devices. But there is no report on the significant temperature effect on the resistive switches of polymer:nanoparticle resistive switching devices in literature.

This paper reports the significant temperature effect on the resistive switches of polymer:nanoparticle devices for the first time. Au NPs capped with conjugated 2NT (chemical structures shown in Scheme 2), are used as the active material in these devices. The resistive switches are significant at room temperature, whereas they become insignificant at low temperature. This is ascribed to the temperature effect on the charge transport through the interface between the Al electrode and Au NPs.



Scheme 1. Interface between a bulk Al electrode and a Au NP capped with conjugated 2NT. The arrow indicates the electron transfer from Al through the capping ligand, 2NT, into the core of the Au NP. WF is for work function, HOMO and LUMO are for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively.

2. Experimental

2.1. Materials and chemicals

All the chemicals, including 2NT, were purchased from Sigma–Aldrich. Gold NPs capped with 2NT (Au-2NT NPs) were synthesized according to literature [43]. In a typical experiment, 0.62 g $HAuCl_4 \cdot 3H_2O$ was dissolved in 50 ml water. It was subsequently mixed with 160 ml *p*-xylene solution of 3 g tetraoctylammonium bromide. The organic phase was collected, and 0.267 g 2NT was added. 50 ml aqueous solution of 0.76 g $NaBH_4$ was then dropwise added under vigorous stirring at room temperature. The solution color changed to black, which indicated the