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Organic bistable memory device from natural rubber (*cis* 1,4 polyisoprene)/fullerene nanocomposite thin films

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ABSTRACT

Memory devices based on C_{60} fullerene molecules and a polydiene, *cis* 1,4 polyisoprene (natural rubber) are described and their current bistability and switching characteristics during write–read–erase cycles are discussed. It is found that natural rubber nanocomposite with a fullerene content even as low as 0.1% exhibit bistability and switching behavior. Multiple tunneling and coulomb blockade effect along with dipolar carrier trapping are identified as the possible reasons for this current bistability.

1. Introduction

Organic Electronics is fast emerging as a major facilitator for information technology with many devices structures exhibit switching characteristics. Organic and polymeric memory devices based on resistive switching [1] as well as floating gate OFETs [2] are becoming popular. The role of fullerene (C_{60}) and its stable derivatives with its large electron affinity is now well established and become an integral part of organic memories. Reports [3] on the memory effects of various polymer composites with fullerenes like poly vinylphenol (PVP), poly vinyl alcohol (PVA), polymethyl methacrylate (PMMA) etc. are already available. However *cis* 1,4 polyisoprene (NR) which is a natural polymer known for its versatility and easy processability is for the first time investigated as an organic memory component. Though a typical non conjugated polymer, it has been well established [4–6] that *cis* 1,4 polyisoprene could easily be doped to have intrinsic conductivity. Further it has been shown that fullerene could be functionalized with NR molecules. Also possibility of C_{60} playing the role of an acceptor of electrons from rubber makes C_{60} play also the role of a dopant for rubber. In this paper we report for the first time the electrical bistabilities and the memory stabilities of Organic Bistable Devices (OBDs) fabricated utilizing C_{60} molecules embedded in a NR layer. The dependence of bistability on the concentration of the C_{60} molecules embedded in the NR layer for the fabricated OBDs is also investigated. The switching characteristics are evaluated to investigate the operating performance of the OBDs. Further, carrier transport mechanisms for the fabricated OBDs are described on the basis of the current voltage (I–V) data.

2. Materials and methods

Natural rubber is a hydrocarbon polymer (*cis* 1,4 polyisoprene) occurring as a milky emulsion in the sap of the three called *Hevea brasiliensis*. Fresh latex collected from rubber plantation contains only 30–40% dry rubber content, balance being mainly water. It cannot be used directly for manufacturing any rubber products. There are different methods to concentrate the rubber latex which contains Dry Rubber Content (DRC) of up to 60% and this forms a technically specified high quality raw material for manufacturing purposes. By proper drying of this latex dry raw rubber is produced. We have used high quality dry rubber in the form of solid lumps supplied by the Rubber Research Institute of India. Natural rubber is known for its versatile properties of flexibility, easy processability, and mechanical properties. C_{60} fullerene (bucky ball) has the structure of a closed cage with 60 carbon atoms in one molecules and is a known for its strong electron accepting property.

The memory devices are fabricated with a cross bar architecture with the active organic composite in between two Aluminum (Al)

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electrodes (Fig. 1). A pattern of Al bottom contact electrodes of width 300 μm are deposited onto well cleaned glass substrates by thermally evaporating Al through a shadow mask. Parent solutions of NR in toluene (concentration 10 mg/mL) and C_{60} in toluene (concentration 2 mg/mL) are used to prepare the NR:C_{60} nanocomposites. The weight percentage (wt.%) of C_{60} in NR here are 0%, 0.1%, 2%, 4%, and 10%. The C_{60} particles dissolved in toluene and sonicated in a bath for 30 min before the solution is mixed with NR/toluene solution. The final composite solutions are stirred violently for about one day to obtain uniform and stable composite dispersions. NR:C_{60} films are coated from solutions of different wt.% by spin coating on the patterned Al electrode coated glass substrates. The devices are finally completed by depositing similar Al electrodes on the organic layer again by thermal evaporation through shadow mask in a perpendicular direction to the bottom Al electrodes, completing the cross point architecture with micrometer dimensions. A similar set of devices are fabricated with top electrode contact formed by pressing pre Al coated glass substrate against the active layer structure coated over the bottom electrode surface. Four similar devices from separate solutions with 0 wt.% of C_{60} in NR (NR only device), 0.1 wt.% of C_{60} in NR (0.1 wt.% C_{60} device), 2 wt.% of C_{60} in NR (2 wt.% C_{60} device), 4 wt.% of C_{60} in NR (4 wt.% C_{60} device), 10 wt.% of C_{60} in NR (10 wt.% C_{60} device) are fabricated with the same structure (Al/NR:C_{60}/Al) and same thicknesses. Keithley 2400 programmable source meter was used to perform the electrical characterization of the device. Similar electrical properties are observed upon changing the polarity between the top and bottom electrodes. Optical absorption spectra of solutions of different wt.% are measured with an Avantes make spectrophotometer.

3. Discussion

The optical absorption spectra of NR:C_{60} composite solutions having different C_{60} concentration clearly indicate the presence of C_{60} as shown in Fig. 2. The peaks in the wavelength range 280–400 nm are attributed to C_{60} absorptions. At higher concentrations of C_{60} a small peak is found to form at 405 nm and this is indicative of the C_{60} doping of polyisoprene, however small it may be and introducing conjugation in minute degrees into polyisoprene chains by the covalent addition of Bucky balls to polyisoprene. The electron accepting C_{60} in all probability form charge transfer complexes with isoprene units thereby increasing the electrical conductivity of the composites. It is seen that the resistance of the composite films decreases by six orders and this must not have been possible with simple percolation effect of the C_{60} particles.

Fig. 3 shows the representative current voltage (I–V) curve for the device, Al/C_{60} 10 wt.%/Al. while Fig. 4(a–e) shows I–V curves for all the five devices fabricated with various NR/C_{60} composites

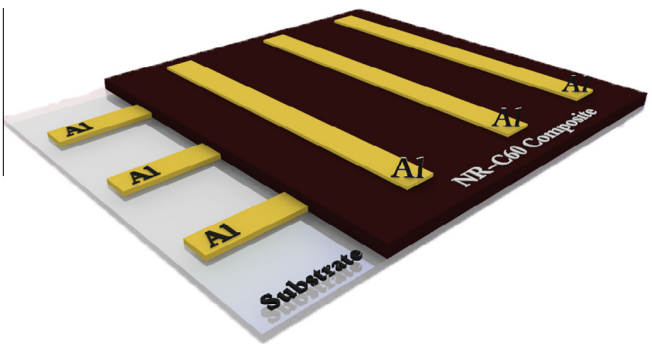

Fig. 1. Schematic diagram of Al/C_{60}:NR/Al device.

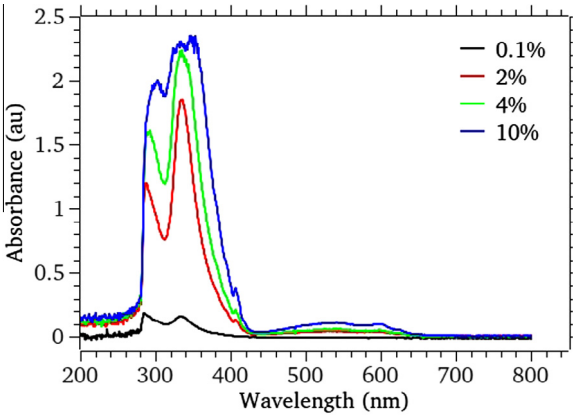

Fig. 2. Optical absorption spectra of Nr:C_{60} solutions.

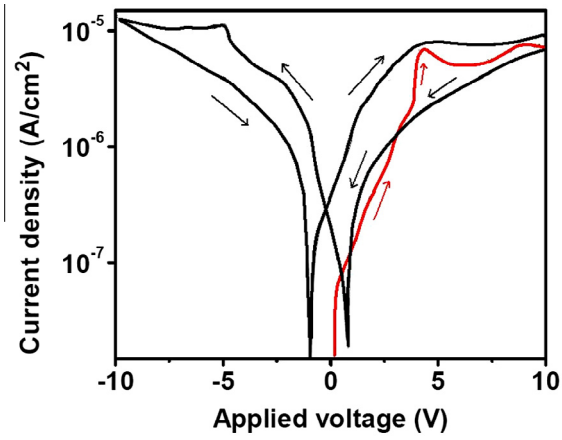

Fig. 3. Representative current–voltage curve for [Al/NR:C_{60} (10 wt.%)/Al] device.

[Al/C_{60} (0.1, 2, 4 and 10 wt.%)] under a voltage sweep of 0.1 V in a cycle from 0 to 10 V, 10 to −10 V, and −10 to 10 V, respectively. All the curves except that for NR alone device (Fig. 3(a)) exhibited clear hysteresis. Current hysteresis behavior is an essential feature of a memory devices. In the case of the NR alone device the hysteresis is not discernible or negligibly small indicating the role of C_{60} in producing the hysteresis. Further all the devices showed symmetrical I–V characteristics for applied voltage sweeps in both directions. The ON and OFF states represent [1] relatively high conductivity and low conductivity of the OBDs, respectively. It is observed (Fig. 3) that the current values are higher for the voltage up-sweep than that for the down-sweep. This type of a current variation is generally different from the usual metal organic metal devices. However there is a report of similar [1] observance for a PVP-C_{60} memory device. Though weak there do exist indications of threshold voltage in the curves, especially for those with higher C_{60} composites. There is about one order of difference in the maximum current values for all most all hysteresis loop and this occurs at applied voltages less than 5 V. This difference in current values is enough for the device to facilitate the usual memory operations of write, read, and erase. The conductivity of the device becomes low immediately after erasing voltage is applied. Further the I–V curves exhibit symmetrical characteristics for both positive and negative applied voltages applied and different contact areas indicating [7] bulk limited transport.

Further short circuit current is visible at 0 V in all composite devices as in the case of similar organic devices and this could be traced [1] to the screening effect on the applied voltage due to