Organic Memory Devices Using C_{60} and Insulating Polymer

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ABSTRACT

In this paper, we describe an all organic molecular memory device that combines the advantages of molecular and organic electronics. We accomplish this by combining C_{60} molecules with poly(4-vinylphenol) (PVP) and co-dissolving them in iso-propanol. The current-voltage measurements show a large hysteresis in the blend devices, in contrast to pure PVP devices. The thin blend films have been thoroughly characterized using Raman spectroscopy, atomic force microscopy and scanning electron microscopy.

INTRODUCTION

The ease of fabrication and use of inexpensive substrates has generated tremendous interest in organic electronics [1 and references there in] while molecular electronics offers the potential of miniaturization down to a few atoms. However, unlike organic electronic devices, molecular devices are difficult to assemble making mass production impossible using existing technology. Although several types of single molecule devices have been demonstrated, molecular memories have shown promise towards technological feasibility [2]. In contrast, there have been relatively few reports of organic memory devices, although recently they have received higher profile [3-6]. A recent article by Scott [3] raises several issues related to emerging memory devices technology. He argues that although there is a clear demand for the next generation of non-volatile solid state memories, the newcomer memory devices must exceed the existing speed and cost constraints of today's entrenched technologies. In addition, the new technology must also meet other critical performance criteria such as long term data retention (at least 10 years and up to 100 years for archiving), low power consumption (a few milliwatts or less for flash type of memory which is equivalent to 1nJ to write and 1pJ to read per bit) and large number of rewrite cycles (Flash memories are rated for 10^6 cycles while DRAM are rated for $> 10^{15}$ cycles).

We propose the development of an all organic memory device that combines the advantages of molecular and organic electronics. Specifically, we have demonstrated non-volatile memory devices using C_{60} fullerene molecules dispersed in an semi-insulating (poly(4-vinylphenol) [PVP]) polymer. Our work shows that the devices exhibit high and low conductance states, rapid switching, low power consumption, long term cycling stability and data retention which renders them suitable for membership in the class of non-volatile, high speed and inexpensive memory devices. The devices can be fabricated at room temperature using spin coating and therefore are easily scalable for mass production.

EXPERIMENTAL DETAILS

PVP polymer is electrically semi-insulating and easily dissolves in isopropyl alcohol at ratio of 25mg to 1ml. The C_{60} fullerene molecule is a closed cage molecule with a precise diameter (0.72 nm) consisting of 60 carbon atoms and is co-dissolved with PVP. Both PVP and C_{60} were obtained from Sigma Aldrich at 99.9% purity. Our macroscopic memory devices (~4mm^2) are fabricated by first thermally evaporating 2mm Al strips (bottom contacts) onto a clean glass slide at a pressure of $1\text{x}10^{-6}$ Torr. Next a solution of PVP and 5 wt % C_{60} was spun on at 7400 RPM and allowed to dry. Finally, 2mm strips of Al (top contacts) were thermally evaporated perpendicular to the bottom contacts. The result is a MIM (metal-insulator-metal) structure, utilizing a cross-point array architecture. The spin coated organic films are well adhered and stable for several months. The film thickness was 30 nm as determined by a Digital Instruments Nanoscope atomic force microscope (AFM) in tapping mode at a frequency of 0.3 kHz. The incorporation of C_{60} in our blend films was confirmed by monitoring the tangential Raman mode of C_{60} near 1469 cm^{-1} with a Renishaw System 1000 instrument using a Peltier cooled CCD and a 785 nm laser with a 2µm spatial resolution.

Current vs. Voltage (I-V) measurements were performed using an Agilent 4156C semiconductor analyzer at room temperature in atmosphere. Dynamic response was measured using a 2020 Data Precision Arbitrary Function Generator and an Agilent 54622A (100Mhz) oscilloscope. The current was measured by monitoring the voltage across a 1 MΩ resistor connected in series with our device. All instruments are computer controlled through a GPIB connection.

RESULTS

The chemical structures of the PVP polymer and the C_{60} fullerene molecule are shown in Figure 1a (i and ii). Measurements using AFM show a surface roughness of 3-5 nm, indicating that our films are smooth. Pure PVP films do not show any surface texture and appear uniform and flat throughout (Figure 1b). The incorporation of C_{60} into the polymer leads to the formation of spirals on the surface (Figure 1c). The overall roughness, however, of the blend film containing C_{60} did not vary significantly from pure PVP. No pin holes or large aggregates of C_{60} are detected in our devices, indicating that the blend is homogeneous. The existence of C_{60} in our blend was confirmed by the presence of the tangential Raman mode for C_{60} in the Raman spectra (Figure 1d). The pure PVP contains small peaks at low wave-numbers but the 1469 cm^{-1} tangential mode peak is absent while the blend material exhibits a combination of PVP and C_{60} peaks. The uniformity of the C_{60} distribution was confirmed by taking a Raman map of the sample surface.

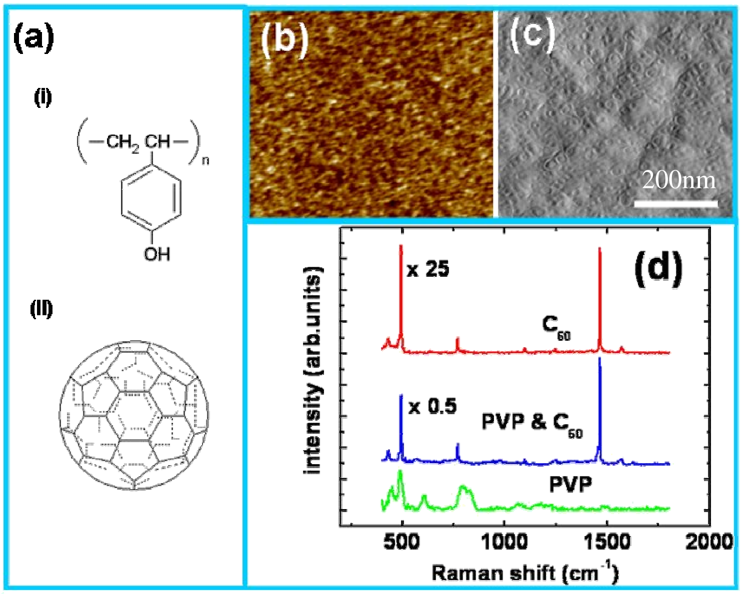

Figure 1. (a) The structure of (i) poly(4-vinylphenol) (PVP) and (ii) fullerene (C_{60}) molecules. AFM images of (b) PVP polymer and (c) PVP + C_{60} blend layer surfaces. (d) Raman spectra of PVP, pure C_{60} and PVP+ C_{60} blend thin films on quartz substrate.

Our devices are analogous to inorganic memory devices where charge storing nanoparticles (such as Si or Ge) are incorporated into an insulating matrix (such as SiO_2) [7]. Such inorganic devices are expensive to fabricate and control of nano-particle uniformity is an issue. The advantage of our devices is that we are able to precisely control the dispersion and concentration of our charge storing C_{60} molecule with the semi-insulating polymer. Furthermore, fullerenes have a constant diameter and readily accept electrons. Thus fabrication of uniform devices in a repeatable manner is possible. Therefore, our devices allow us to take advantage of molecular storage capability of the fullerenes, significantly enhancing the storage density capability

The schematic of the memory device is shown as an insert in Figure 2a. Typical current-voltage *(I-V)* measurements of Al/PVP/Al and Al/PVP+C_{60}/Al structures exhibit symmetrical characteristics for negative and positive applied voltages and different contact areas (Figure 2a), indicating bulk-limited transport. Thus, contact interface does not play any significant role in determining the electrical behavior of these devices. Therefore, we can state that our devices do not exhibit rectification. The pure PVP layer does not show significant hysteresis with increasing and decreasing voltage. In contrast when C_{60} is incorporated into PVP, a hysteresis is observed. Note that in contrast to hystereses observed in defective polymers such as pentacene, the hysteresis in our material persists whether the measurements are made at fast (μs) or slow (several seconds) voltage sweeps indicating the hysteresis is due to charge injection and retention within the C_{60} molecule and not due to traps or other defects. The hysteresis is sufficiently large, with the maximum difference between the current levels being approximately 150 nA at 1.5 V.

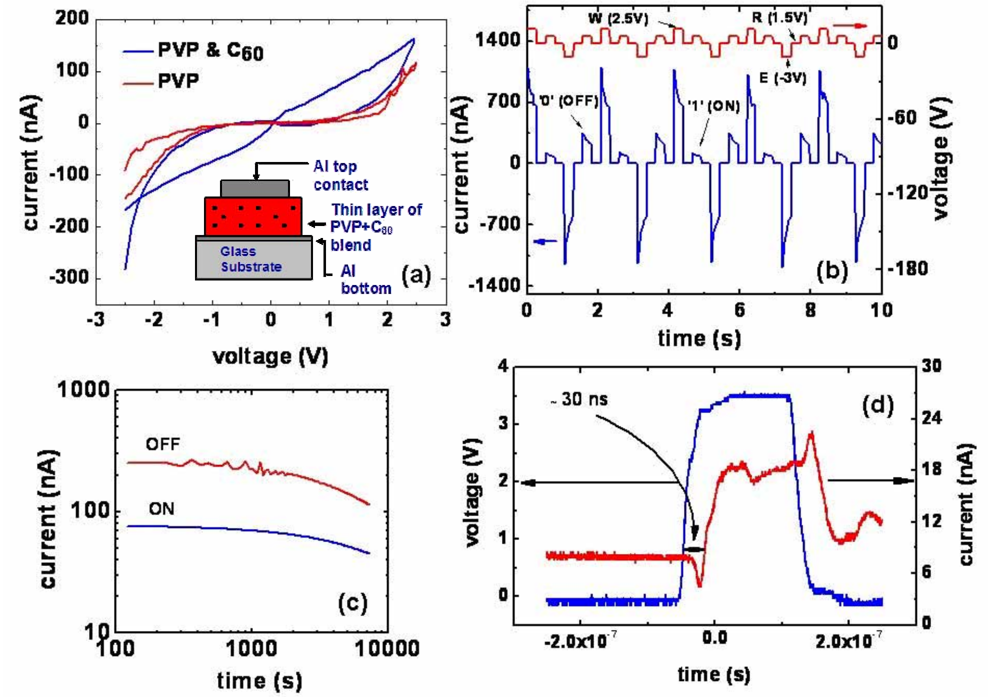

Figure 2: (a) Current versus Voltage characteristics of single layer devices of pure PVP (no hysteresis) and PVP containing C_{60} (hysteresis). Schematic of MIM device is shown in insert. (b) Memory response of the devices during write-read-erase-read voltage cycles. (c) Data retention graph showing a consistently higher current value for the OFF state than for the ON state. (d) Electrical delay time measurements indicating a response time of 30 nanoseconds.

In order to translate the *I–V* hysteresis into memory operations, we have measured the read-write-erase cycles of our devices (Figure 2b). The device can be tuned from high ('0' OFF state) to low ('1' ON state) conductivity state by applying +2.5 V (comparable voltages to Flash memory devices) to negatively charge the C_{60} molecules. This can be registered as the 'write' step. Then by applying +1.5 V, the current can be recorded (read step). The negatively charged C_{60} molecules screen out part of the applied electric field, thus lowering the conductivity. Once written, the device is stable in this state for several months because the energy barrier between PVP and C_{60} is large enough to prevent electrons from tunneling out of the C_{60} molecule. The device can be fully erased by applying -3.0 V to remove the stored electrons from the C_{60} molecules and return the device to its original OFF state. This state can then be read by applying +1.5 V. The energy dissipation in our memory is estimated to be about 0.01pJ per bit with the 30ns delay time to read and 0.1pJ per bit to write. These values are favorable with existing flash memory devices. The robustness of our devices was tested by monitoring both ON and OFF state currents under continuous voltage as a function of time. No deterioration of the performance was observed for up to 1 hour (Figure 2c). After an hour there was a slight decline in both ON and OFF states for the next hour. However, the difference between the ON and OFF states always remained constant. It should be remembered that continuous two hour testing of the ON and OFF states translates into substantially long time since a single read-write-erase cycle is only few tens of nanoseconds. In order to investigate the stability of our devices, we monitored their performance over several months. No significant deterioration of device performance was observed for devices stored in normal laboratory conditions (~ 45% humidity, 22°C) for up to six months. In addition to durability and power consumption, delay time is an important parameter which determines the read/write speed of the devices. The response time was measured and found to be ~ 30 ns (Figure 2d), which is close to the limit of our measurement apparatus when taking inductance from the circuitry into account. Although 30 ns is sufficiently fast for memory devices, we believe that we can improve on this by optimizing the device parameters since charge transfer into C_{60} from conducting polymers has been measured to occur on the order of a few hundred femto-seconds [8]. The delay time in nano-seconds suggests that we are able to read-write-erase the information in nanoseconds and make the information access time of these devices close to DRAM

CONCLUSIONS

In brief, we have successfully demonstrated a high speed, economical, low power consuming all-organic molecular memory device. The memory devices are unique in that they combine the low fabrication cost advantages of organic electronics and the miniaturization advantage of molecular electronics. The use of C_{60} molecules as the charge storage medium and the ability to disperse them uniformly in an insulating polymer matrix using a solution based (wet) technique holds promise for high storage density devices.

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