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Non-volatile memory device- using a blend of polymer and ferroelectric nanoparticles

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In recent years, the interest in the application of organic materials in electronic devices (light emitting diodes, field effect transistors, solar cells), has shown a rapid increase. A new family of organic electronic device is organic memory device. These devices, based on a thin film of nano-sized particles and small molecules emblebded in an organic layer attracted considerable attention. This work presents the polymer memory device which is made of a blend of poly(vinyl acetate) and ferroelectric barium titanate nanoparticles. A polymer blend of polyvinyl acetate and barium titanate ($BaTiO_3$) nanoparticles was prepared in methanol and spin coated onto a glass substrate marked with thin Al tracks and top contacts were evaporated onto the blend after drying - this resulted in a metal-organic-metal (MOM) structure. The current-voltage (I-V) behaviour of MOM devices shows that the devices can be switched from a high conductivity state to a low conductivity state, by applying an external electric field - this property can be exploited to store data bits. The working mechanism, in these devices is based on ferroelectric properties of barium titanate.

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Keywords: Ferroelectric, Memory devices, Switching mechanism

1. Introduction

Organic materials exhibit strong potential to be active materials for electronic devices in future electronic industries. In recent years there has been a growing interest in worldwide in the field of organic materials and organic electronics as low cost, easily processable alternatives to conventional inorganic semiconductors [1, 2]. There has been a number research efforts to make reliable light emitting diodes and thin film transistors using organic materials but not much efforts have been put to .organic memory devices and their working principle(s). Here, we report further understanding of the working principle of polymer memory devices.

Reversible electrical switching and memory effect has been reported for a range of organic materials and device configurations [3,4]. Electrical switching has been observed in various organic materials, including polymers and an admixture (a blend) of small organic molecules and/or nanoparticles in a polymer matrix. The polymer memory devices can be switching between two conductivity states upon to application of electric field [5]. The fundamental structure of the organic memory devices consist of cross-point elements with two parallel top and bottom electrodes between the active organic materials. Most recent research activity focuses on the find the nano-size particles with very interesting proprieties which can be used in polymer matrix to realize memory device.

Ma *et.al* have been exploring the organic memory devices based on a thin films of metallic nanoparticles embedded in an organic layer. The organic memory has a nanoseconds writing time and exhibits the non-volatile memory effect, which makes it ideal for applications similar to flash memory [6]. F.Li and co-workers [7] demonstrated the electrical bistability of the memory device based on ZnO nanoparticles embedded in a polyamide (PI) layer. The use of gold nano-particle (encapsulated in organic ligands) in hybrid organic/inorganic memory devices has been demonstrated by Paul et.al [8,9] and Kolliopoulou et. al [10]. Memory device with gold nanoparticles embedded in a polymer matrix have also beed demonstrated by Quyang et.al [11] and Prakash et al [12]. Also, a polymer memory device has been reported by using mixture of gold nanoparticles (GNPs), 8-hydroxyquinoline (8HQ), and polystyrene (PS) [9,13,14]. The 8HQ serves as the electron donor, the GNPs serve as electron acceptor, and PS only serves as matrix and plays no role in the memory effect. The memory effect in device consisting of an organic insulator and C_{60} molecules have been demonstrated by Paul et al. [15]

In this article, we described a memory effect in devices consisting of an organic insulator (PVAc or PS) and barium titanate nano-particles.

2. Experimental

As purchased barium titanate nano-powder (from Sigma Aldrich) has the cubic phase and $BaTiO_3$ with cubic structure does not have ferroelectric properties. The $BaTiO_3$ powder was annealed in air at 1000^0C for one hour to obtain the tetragonal phase and which exhibit ferroelectric properties. The phase change, due to higher temperature annealing, is confirmed by powder x-rays diffraction analysis.

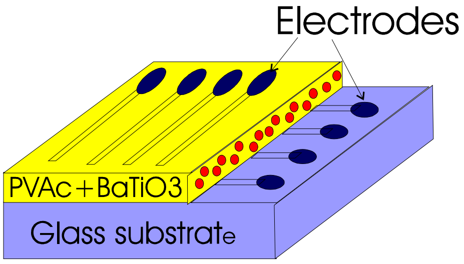
For MIM structure a polymer blend is prepared by dissolving barium titanate nanoparticles and PVAc in methanol. To obtain the homogeneous mixture, the blend was kept in the ultrasonic bath for an hour. The blend was spin coated onto different glass substrates marked with thin Al tracks and a top contact was evaporated on to the blend after drying - this resulted in a metal-organic-metal (MOM) structure.

The polymer blend for MIS structures is prepared by dissolved barium titanate nanoparticles and polystyrene in dichlorobenzene. The MIS (metal/ insulator/ semiconductor) structures investigated consisting of an ohmic bottom Al contact to p-type Si, polymer blend (barium titanate and polystyrene) followed by the deposition of polyvinyl acetate and top aluminium electrodes.

The current voltage and memory retention behaviour of the MOM structures were measured in a screened sample chamber in the dark and at room temperatures, using a PC-driven pico-ammeter (HP4140B). The capacitance-voltage measurements were conducted on an HP 4192A impedance analyser at a frequency of 1 MHz.

3. Results and discussion

The structure of the devices used for current- voltage investigations are shown in Fig.1. The device used for I-V measurements have the architecture of a single layer sandwiched between two metal electrodes. The active layer of these devices contains ferroelectrical barium titanate nanoparticles in PVAc.



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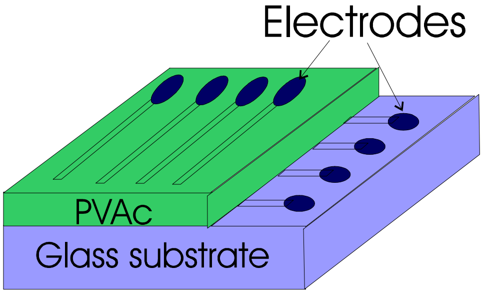

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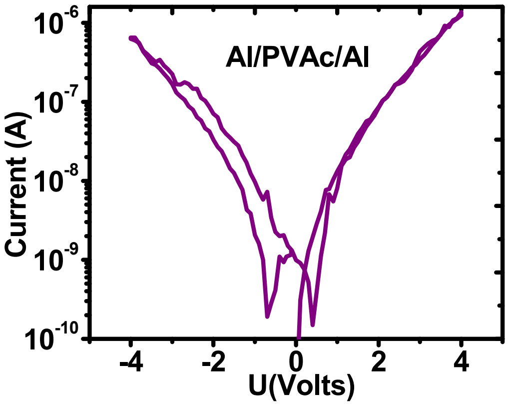
Fig.1. Schematic structure of (a) pristine PVAc; (b) PVAc+$BaTiO_3$.

The metal-PVAc-metal structure was investigated to check if the incorporation of barium titanate nanoparticles has any influence on the switching behavior.

The typical I-V behavior or the Al/PVAc/Al and Al/PVAc+$BaTiO_3$/Al structures are presented in Fig.-2. From these characteristics, it is evident that barium titanate nano-particles play a significant role in determining the electrical behvaiour of these devices. The structures exhibit symmetrical I-V characteristics for negative and positive applied voltage. The symmetrical I-V characteristics are typical of a bulk-limited mechanism. The Al/PVAc (or Al/PVAC+$BaTiO_3$) interface does not play any significant role in determining the electrical behavior of these structures.



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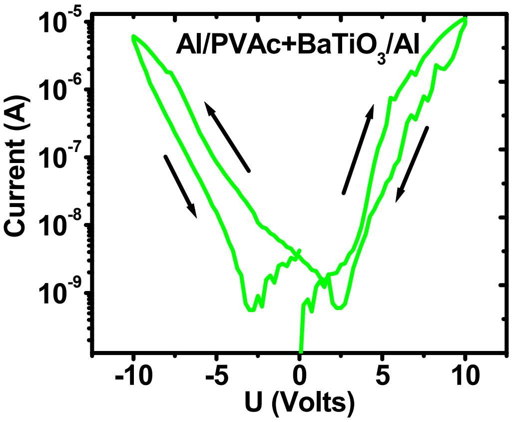

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Fig. 2. I-V characteristics of (a) Al/PVAc/Al and (b) Al/PVAc+$BaTiO_3$/Al.

The observed I-V behaviour in our devices leads to conclude that the switching mechanism in our devices is associated with ferroelectric properties of barium titanate nano-particles. It is well known that the $BaTiO_3$ with tetragonal phase has the ferroelectric properties. The barium titanate consists of a number of electric domains, and in the absence of the external field, each domain has dipole moments oriented in random directions. These electric domains can be aligned in the same direction when an external electric field is applied.

The switching between two conductivity states depends upon the direction of the internal electric field originated from the ferroelectric behaviour of the $BaTiO_3$ nano-particles. If the interal electric field is in the same direction with the applied electric field we get higher conductive state and lower conductive state if the internal field in opposite direction,

Memory retention time (Fig. 3) was also investigated, for admixture of PVAc and $BaTiO_3$. The devices exhibit a distinguishable high and low conductivity states for over 10,000 cycles over a period of 4 hours.

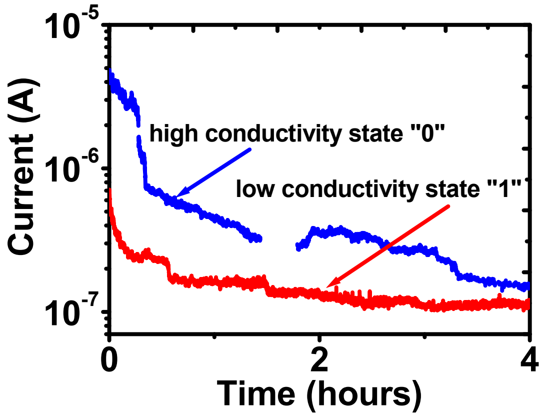
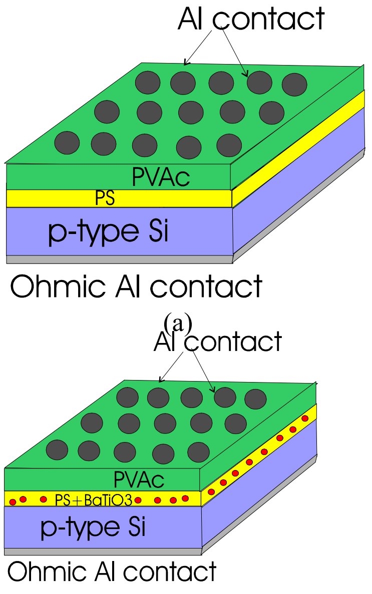


Fig.3. Retention time of Al/PVAc+$BaTiO_3$/Al device.

In order to confirm that the ferroelectrical barium titanate nanoparticle play significant role in switching mechanism in our devices we have investigated the capacitance versus voltage (C-V) behaviour of metal-insulator-semiconductor (MIS) and their structures shown in Fig,-4

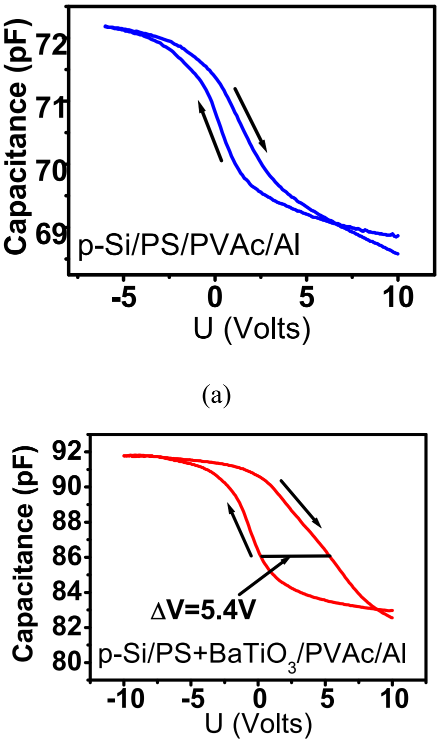


(a)

(b)

Fig. 4. Schematic structure of metal-insulator-semiconductor devices for C-V measurements (a) Al/PVAc/PS/Si, (b) Al/PVAc/PS+$BaTiO_3$/Si.

The C-V data for the two different device structures investigated are shown in Fig.-4. The C-V behaviour for both structures investigated show accumulation/depletion/inversion characteristics associated with MIS structures.



(a)

(b)

Fig. 5. C-V characteristics of (a) Al/PVAc/Al and (b) Al/PVAc+$BaTiO_3$/Al.

The hysteresis loop indicated the dipole rotation in ferroelectric crystalline domains when the high electric field of opposite polarity is applied.

The MIS devices made of PS and PVAc layers (Fig. -4a) shown a small hysteresis (1.2V) while the (Fig.-4b) MIS devices with PVAc/PS+$BaTiO_3$ show a hysteresis with a threshold voltage of 5.4V indicating that the electric domains determine the switching behavior in these devices.

4. Conclusion

The polymer memory devices based on blend between a barium titanate nanoparticles and a polymer (PS and PVAc) were investigated. Both, current-voltage and capacitance-voltage measurement prove that ferroelectrical nanoparticles play a crucial role in the switching mechanism in our devices. We proposed that the working mechanism – switching between high to low conductivity state is completely determined by the value of the internal electric field.

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