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Filament theory based WORM memory devices using aluminum/poly (9-vinylcarbazole)/aluminum structures

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Aswin Suresh[a], Govind Krishnakumar[a], Manoj A G Namboothiry[*a]

Spin coated poly(N-vinylcarbazole) (PVK) sandwiched between thermally evaporated aluminum (Al) electrodes on a glass substrate showed unipolar Write Once Read Many times (WORM) characteristics. The pristine devices were in the low resistance ON state exhibiting ohmic behavior and at a voltage near -2V, they switched abruptly to the high resistance OFF state showing space charge limited current (SCLC). We suggest that the rupturing of metallic filaments due to Joule heating may explain the effect. The WORM devices exhibited an ON/OFF ratio of 10^8 , retention of 1000 s and endurance of ~10^6 cycles in both ON and OFF states.

Memory devices are essential parts of almost all electronic devices. Organic material based memory devices have several advantages such as low cost fabrication methods, simple device structure, low power operation and flexibility,[1,2] compared to currently used inorganic materials like silicon. WORM is one type of memory device, which is used for permanent data storage application such as archival storage of images and for noneditable databases. Even though, there are many reports of WORM devices based on organic materials, organic inorganic hybrid structures, the mechanism of WORM property is a matter of debate and it depends on many processing conditions especially in the case of organic polymers.

PVK is an organic polymer commonly used as hole transporting material in organic optoelectronic devices and it can be processed in different organic solvents to form thin films using spin coating. There have been many previous reports on resistive memory devices based on PVK and its derivatives in different metal/polymer/metal device structures.[3-7] In previous studies, Al/PVK/Al structure showed reversible bistable resistive switching and the ON and OFF states were explained based on charge trapping and detrapping in PVK.[4]

In our present study, the polymer PVK was processed in chloroform and sandwiched between two Al electrodes, on a plain glass substrate, different from previously reported studies, where PVK was processed in 1,2 dichloroethane to form Al/PVK/Al structure. This resulted in a WORM device unlike the previously reported reversible bistable resistance switching for the same device structure. The results show that there is no uniqueness in the device working for the same metal/polymer/metal structures and it all depends on the processing condition and electrical transport properties of the polymer. We propose that the pristine devices are in a high conductance state due to the presence of filaments formed during deposition of the top metal electrode, and they switch to a low conductance state due to the Joule heating induced rupture of the filaments, which are different from previously reported working mechanisms for WORM devices using PVK.

The Al/PVK/Al structure was chosen due to its simple device fabrication process. PVK films can be easily obtained by spin coating and it is suitable as a hole transporter.[8] Al is a much cheaper alternative to indium tin oxide (ITO) as the bottom electrode. To get high ON/OFF ratio, we used chloroform as the solvent for PVK during spin coating, as such films were reported to have more surface roughness and support a higher current, as compared to other solvents.[9] The solubility of PVK is also very high in chloroform.[9]

For fabricating the devices, plain glass slides of dimensions, 2 cm x 1.5 cm were cleaned by ultrasonicating sequentially in detergent, distilled water, acetone, isopropanol and methanol for 20 minutes each. They were then dried in a vacuum oven at 40

°C overnight. The dried slides were cleaned using UV-Ozone cleaner for 20 minutes. The cleaned slides were coated with Al (the bottom electrode), in a thermal evaporator, at a pressure of 7 x 10^{-6} mbar, using a shadow mask. The thickness of the layer was approximately 120 ± 10 nm.

PVK (average M_w ~1,100,000, T_g – 220 °C) obtained from Sigma-Aldrich, was added to chloroform and stirred for 20 minutes to get a solution of 5 mg/ml, which was spin coated on to the slides at 3000 rpm resulting in a uniform coating of approximately 130 ± 10 nm thickness. The spun coated slides were kept in a vacuum oven at 90 °C for 20 minutes. This thickness was optimized after trying WORM devices with PVK thin films of thickness varying from 50 nm to 200 nm.

The PVK coated slides were coated with Al (top electrode), in a thermal evaporator, at a pressure of 7 x 10^{-6} mbar, using a shadow mask. The thickness of the layer was approximately 120 ± 10 nm. The area of an individual top electrode (the active area of a device) was 16 mm^2 (4mm x 4mm). The devices were also made with different electrode areas to study the dependence of ON and OFF state resistance on the device active area. Inorder to test the consistency of our results, we have made more than 200 devices for the current studies.

The devices were characterized using a Keithley 4200-SCS Semiconductor Characterization System. All measurements were taken in ambient conditions. Two-terminal current voltage (I-V) test was carried out. Typically, the devices were swept (with respect to the bottom electrode) from 0 to -5 V, and -5 V to 0 V. The current was also measured against time at a fixed voltage, at -1 V (ON state) and – at -3 V (OFF state), using a Keithley 6430 source meter.

An external applied voltage was swept from 0 V to -5 V and then -5 V to 0 V keeping different levels of current compliance (25 mA, 50 mA, 75 mA, 100 mA). The devices initially were in a high conductance (ON) state. For a current compliance of 100 mA, as the voltage was increased the current increased till at a certain voltage, near -2 V, the current dropped abruptly by several orders of magnitude and the devices switched permanently to a low conductance (OFF) state. Figure 1a shows a typical I-V characteristic of the device. The devices remained in the OFF state for all subsequent sweeps, thus enabling them to be used as WORM devices.

Even though different compliance current condition were used as mentioned earlier, WORM behavior was observed only for a compliance level of 100 mA showing a threshold value of current for writing process. The devices did not show a reversal of the ON state upon reversal of bias (sweeping from 0 V to +5 V and to 0 V) (Figure S1). It is also to be noted that, there was no WORM effect when the top electrode was initially biased '+' ve with respect to the bottom.

Figure 1. (a) Typical I-V characteristics of the Al/PVK/Al devices. (b) log (I) vs. log (|V|) plot to understand the conduction mechanism

To test the retention of the device, the ON state current was measured continuously at a read voltage of -1 V (Figure 2a). The device remained ON for more than 1000 s. The ON state current was typically in the range of 0 – 15mA. On applying a write voltage of -2 V, the current rose to the compliance current value of 100 mA and within seconds, dropped to the OFF state with currents in the range of 10^{-10} A (Figure 2b), thus showing an ON/OFF ratio of 10^8. To test the retention of the OFF state current, a device was written at -2 V and the current was measured continuously at -3 V. The device remained in the OFF state for more than 1000 s (Figure 2a). The endurance performance of the device in both ON and OFF states were measured at -1 V I in the sampling mode and is as shown Figure 3(a). The device showed ON and OFF states with large resistance ratio over 10^8 and exhibited little degradation over 10^6 cycles.

The initial ON state is attributed to the conduction channels caused by the Al filament formation during thermal evaporation in the PVK film and reduced dipole moment due to these filaments in PVK film.[5] It is expected that the metal would diffuse into the polymer layer and form high conductance channels, in the form of filaments especially in the case of PVK processed in chloroform which possess high surface roughness.[9]

Figure 2. (a) Retention data of Al/PVK/Al WORM memory devices in the ON and OFF state and (b) write process at -2 V

It has been reported in a previous work that metals can diffuse inside the polymer layer with the thermal energy present during the deposition of the top electrode.[10] There have been previous reports about this type of diffusion taking place in the case of PVK,[7,11] and the formation of filaments in the PVK layer.[5] An SEM cross sectional image of the device before applying bias was taken for understanding this (Figure S2a), but higher resolution was limited due to the charging of the polymer film. The slope of log (I) vs. log (V) graph is ~1 in the ON state (Figure 1b), which points to ohmic conduction through metallic filaments. This is different from the mechanism proposed for WORM devices using PVK in the ITO/PVK/Al structure,[7] where the work function difference between ITO and Al plays an important role.

Here we explain the I-V characteristic of the Al/PVK/Al structure based on electrical transport properties of PVK, effect of possible Al_2O_3 layer on top of bottom Al electrode and conduction through metallic filaments in the structure. Since we are using similar metals, we expect a symmetric I-V characteristics in the '-' ve and '+' ve bias of the top electrode with respect to the bottom electrode (energy level diagram is as shown in the Figure S3a). Our I-V measurements within the limits of ON state show nearly symmetric I-V characteristic (Figure S3b) for Al/PVK/Al structure. But the observation of an OFF state only in the case of top electrode '-' ve biased with respect to the bottom electrode can be due to the following reasons. Possible formation of the Al_2O_3 on top of the bottom electrode while processing the device and its barrier to electron and hole injection favour the injection of holes and electrons through the top electrode as the governing mechanism of the I-V characteristic. In the case. where the top Al electrode is '+' ve biased with respect to the bottom Al electrode, holes are injected into the PVK, which is a good hole transporting and poor electron transporting material. The net current in this configuration is mostly attributed to the excellent hole transporting properties of the PVK. The Al_2O_3 barrier at the bottom electrode prevents electrons from flowing through the filaments and hence avoiding any metal filament breaking due to Joule heating. This explains the absence of an OFF state in this biasing condition. But in the case. where the top Al electrode is '–' ve with respect to the bottom Al electrode, the injected electrons pass through the filament as it provide a better path way compared to PVK which is a poor electron transporting material. These effects results in more current passing through filaments which are formed in the PVK matrix while thermal evaporation of top electrode as mentioned previously. High current through the metallic filaments results in the high resistant OFF state of the Al/PVK/Al device due to breaking of filaments caused by Joule heating. (a schematic of the filament formation and rupturing resulting in the ON and OFF state is shown in the Figure S4 a and b respectively) This also may results in modification of top Al/PVK interface which further reduces the probability of injection of holes and electrons to the PVK resulting in the device. continuing in the OFF state even during the reversal of biasing. Based on the explanation above, we can conclude that Al/PVK/Al WORM devices show a unipolar nature.

Filament theory, as the proposed mechanism underlying the device operation was further investigated and explained based on the following further evidences. It was observed that devices could not be written at -2 V in the cases where the ON state current read at -1 V attained the compliance current value. This can be due to the presence of a filament that has a low resistance – may be a thick filament, which can carry a current equal to or probably greater than 100 mA without fusing. Therefore such a filament cannot be fused at -2 V since the current passing through it then would also be the compliance current value (100 mA) and require a higher current for fusing. This dependence of the write operation on ON state compliance current has been reported to support filament theory.[12]

Figure 3. (a) The endurance performance of the Al/PVK/Al WORM device in the ON and OFF state and (b) area dependent resistance of ON and OFF state at room temperature and at 85 °C.

Our observation of a threshold value for current compliance also suggests that, at low compliance current there is not enough rupturing of filament to bring the device to OFF state. An area dependant device test (as shown in Figure 3b) found that the resistance in the ON state was independent of area and that in the OFF state was inversely proportional to the area, further giving evidence for a filament model for the device working mechanism. This is an explanantion based on an effective cell area attributed to conducting filament density and diameter rather than to the geometrical size of the electrodes.[13,14] It is also to be noted that resistance measurement carried out at 85 °C (Figure 3b) showed an increase in the resistance for ON state showing the properties of a metal and decrease in resistance in the OFF state showing the properties of a semiconductor. This also confirms the filament formation in the Al/PVK/Al WORM devices. In order to confirm filament theory and its limitations, WORM device were made with different thickness of PVK layer, thickness varying from 50 nm to 200 nm, expecting a negligible chance of filament contribution as the thickness increases to the ON state current. In the case of 50 nm film, we observed a shorting between the two electrodes and in the case of films of 200 nm thickness, there was no observation of high current state. Hence the thickness was optimized for reproducible results around 130 nm and we observed reproducible WORM properties for more than 50 devices made in our lab.

The device attains an OFF state, when a sufficient voltage such as -2 V (write voltage) is applied. This can be due to the joule heating and the filament ruptures caused by the current passing through the filaments, changing the device irreversibly to a low conductance OFF state, much like the operation of an electric fuse. It was estimated from the values of the resistivity, density, specific heat capacity, melting point, etc. of Al, that a current in the range of 10^{-3} A would suffice to melt a nanoscale Al filament, thus causing the transition. PVK would help in the process by reducing dissipation of heat. PVK is also stable as an insulator, even in continuous high temperature use. The top view of the Al through a SEM shows nanodomains, which can be due to Al diffusion into the PVK film during the ON state to OFF state transformation (Figure S2b). We speculate that the breakage of filaments result in metal islands in the PVK film. The current in the OFF state shows a V^2 dependence (Figure 1b) suggesting a space charge limited current in the OFF state.[15] There have been similar suggestions in some previous papers about the conduction mechanism in PVK.[1,16,17]

Conclusions

In conclusion PVK processed in chloroform and sandwiched between Aluminum electrodes showed WORM properties unlike previous reports where such structure processed in solvents other than chloroform showed rewritable bistable memory devices. The results showed that the resistive memory phenomena depend on the processing condition and electrical transport properties of the organic polymer. The ON state was explained based on the filament theory and the OFF state showed a space charge limited current transport behavior. The WORM devices exhibited an ON/OFF ratio of 10^8, retention of 1000 s and endurance of ~10^6 cycles in both ON and OFF states.

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Notes and references

[a] School of Physics, Indian Institute of Science Education and Research, Thiruvananthapuram, CET Campus, Thiruvananthapuram-695016, Kerala, India.
Phone: +91 471 2599426
Fax : +91 471 2597427
Email:manoj@iisertvm.ac.in
*corresponding author.

Electronic Supplementary Information (ESI) available: [I-V characteristic of Al/PVK/Al device with voltage sweeping sequentially from 0 V to _5 V -5 V to +5 V and then +5 V to 0 V; Cross sectional (before biasing) and top electrode view (after biasing) SEM images of Al/PVK/Al device.; energy level diagram of the Al/PVK/Al structure and I-V characteristic of the device within the ON region from -1V to +1V; Schematic of the filament formation and breaking in the Al/PVK/Al structure]. See DOI: 10.1039/

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