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RESEARCH ARTICLE

# Nonvolatile Write-Once-Read-Many Times Memory Devices Based on the Composites of Poly(4-vinylphenol)/Vulcan XC-72

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We fabricated write-once-read-many times (WORM) type organic memory devices in $8 \times 8$ cross-bar structure. The active material for organic based WORM memory devices is mixture of both poly(4-vinyphenol) (PVP) and Vulcan XC-72s. From the electrical characteristics of the WORM memory devices, we observed two different resistance states, low resistance state and high resistance state, with six orders of ON/OFF ratio ($I_{ON}/I_{OFF} \sim 10^6$). In addition, the WORM memory devices were maintained for longer than 50000 seconds without any serious degradation.

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**Keywords:** Organic Electronics, Write-Once-Read-Many Memory, Cross-Bar Architecture.

## 1. INTRODUCTION

Organic-based electronic devices such as organic light emitting diodes (OLED), transistors (OTFT), photovoltaic cells (OPVs), and memory devices promise to organic electronics by providing low cost, light weight, and easy fabrication and that can be also applied to the ubiquitous components that are printed onto flexible substrates.[1–4] Among these organic devices, the organic memory has been studied as an alternative to the conventional inorganic based nonvolatile memory applications.[5–10] Organic memories have been explored using various organic materials such as small molecule system,[11] donor–accepter complex,[12] and nanoparticles blending systems.[13] Particularly, the nanoparticle-blend system for organic memory has been extensively studied since the simple controllable process methods such as various kinds of particles, size difference of particle, and concentration condition of particles.[14–16] Based on these organic systems, two types of organic memory devices have been investigated. One is an electrically write and erasable organic non-volatile memory device. The other one is a write-once-read-many times (WORM) type organic memory device. Among these two types of organic memory devices, due to the rapid and permanent data storage, the organic based WORM memory has been one of the potential candidates for non-editable memory applications, such as electronic barcodes, contactless radio frequency identification (RFID) tags, and throwaway electronic leaflet.[17–21]

In this study, we fabricated organic based WORM memory devices in $8 \times 8$ cross-bar architecture. The active polymer layers are composited a Poly(4-vinyphenol) (PVP) and a Vulcan XC-72 carbon black (Vulcan XC-72s). We report the electrical properties of these WORM memory devices and explain their charge transport mechanisms.

## 2. EXPERIMENTAL DETAILS

The WORM memory devices were fabricated using a mixture of Vulcan XC-72 carbon black particles (Vulcan XC-72s) and poly(4-vinylphenol) (PVP) which is dielectrics (dielectric constant $K = 5$).[22] The Vulcan XC-72s is conducting particles. These are well-known and commercially available material as catalyst loading activities in the direct methanol fuel cell (DMFC) research field. An indium tin oxide (ITO) (sheet resistance of $\sim 8\Omega/\square$)-coated glass substrates were pre-cleaned with a typical ultrasonic cleaning process by acetone, methanol and deionized water in sequence. The patterned ITO with 100 $\mu$m line-width was prepared as bottom electrodes (Fig. 1) by conventional photolithography and a subsequent wet etching process. The PVP (average molecular weight ~20,000) and Vulcan XC-72 were used to make a mixture (PVP:Vulcan XC-72s = 1:5, 1:3, 1:2 and 1:1 solution volume ratios)

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of PVP solution (0.4 g/20 ml) and Vulcan XC-72s solution (0.005 g/30 ml) dissolved in methanol. Then, the PVP:Vulcan XC-72s solution was spin coated at 500 rpm for 5 seconds and 2000 rpm for 35 seconds in sequence in a $N_2$-filled glove box and the thickness of the film was determined to be ~180 nm (measured by Alpha-step). To remove residual solvent from the film, a baking process was performed on a hot plate in the $N_2$-filled glove box at 120 °C for 10 min. Then, aluminum with 8 line patterns of 100 $\mu$m line-width and 50 nm thickness was deposited for top metal electrodes with a shadow mask by an electron-beam evaporator with a deposition rate of 0.3 Å/sec at a pressure of ~ $10^{-7}$ torr.

## 3. RESULTS AND DISCUSSION

Figure 1(a) shows a schematic of the ITO (bottom electrode)/PVP:Vulcan XC-72s (active layer)/Al (top electrode) memory devices in the 8 × 8 cross-bar structure. Figure 1(b) shows an optical image of the memory device, illustrating the PVP:Vulcan XC-72s composite layer sandwiched between ITO and Al electrodes. A schematic cross section view of the fabricated memory devices is illustrated in Figure 1(c). The Vulcan XC-72s, showing the size of 500–700 nm, are dispersed within the PVP matrix, as observed in the transmission electron microscopy (TEM) image (Fig. 1(d)).

Figure 2 shows the current–voltage ($I$–$V$) characteristics of organic based WORM devices. In Figure 2(a), we compared the ($I$–$V$) characteristics of two control devices; a PVP only device and a device with a large amount of Vulcan XC-72s. We swept the voltage from 0 V to +10 V and then 0 V to −10 V to the Al top electrode for these two devices. For the device of PVP only, the current level was found in the range of pA level at 1 V, indicating an insulating behavior. On the contrary, when we increased

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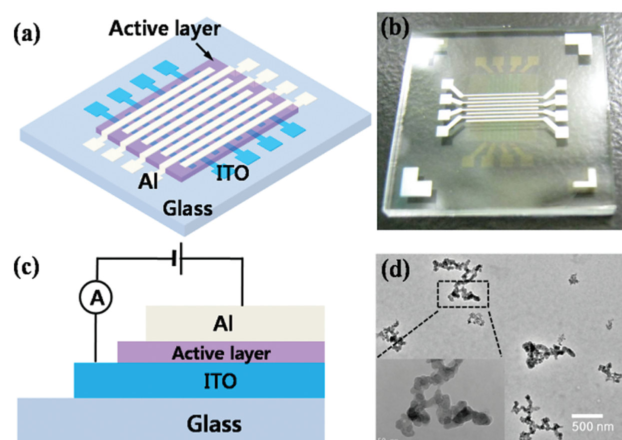


Fig. 1. (a) Schematic and (b) optical image of ITO/PVP:Vulcan XC-72s/Al memory devices in an 8 × 8 array structure. (c) Schematic of the cross-section view of ITO/PVP:Vulcan XC-72s/Al structure. (d) TEM image of a composite film with PVP:Vulcan XC-72s volume ratio of 1:1.

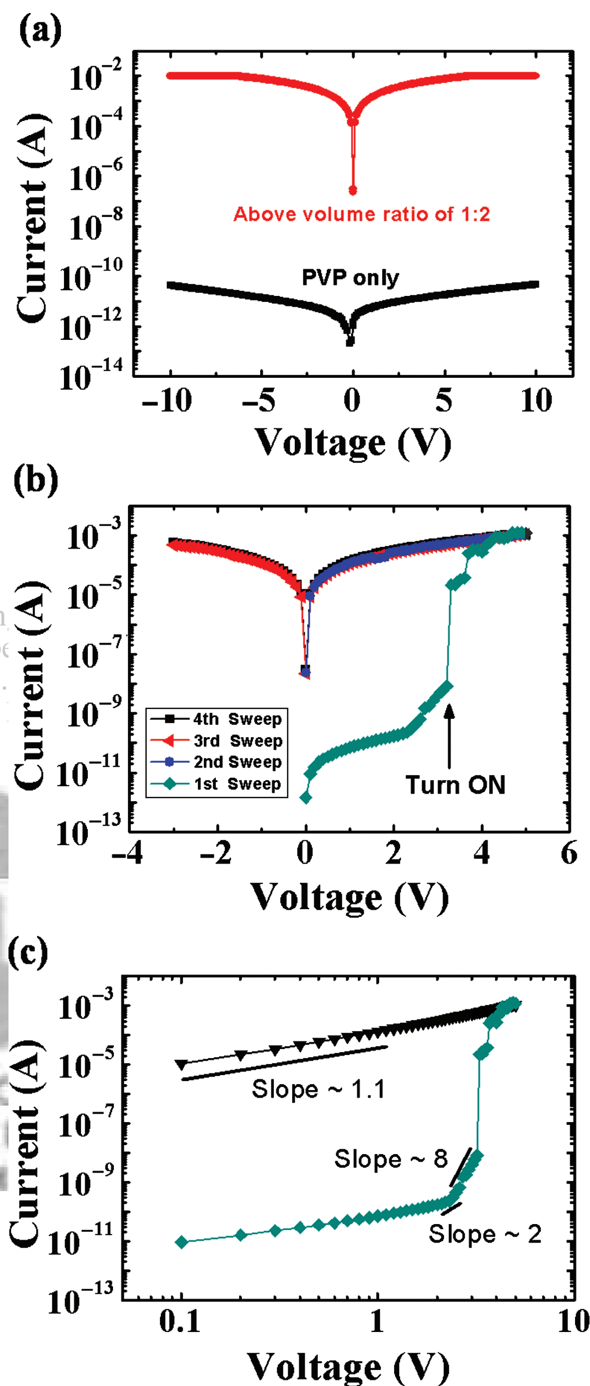


Fig. 2. (a) $I$–$V$ characteristics of a device with PVP only and a device with high Vulcan XC-72s ratio in PVP:Vulcan XC-72s (1:2 ratio). (b) Semilogarithmic plot of the $I$–$V$ characteristics of ITO/PVP:Vulcan XC-72s/Al WORM memory devices with PVP:Vulcan XC-72s volume ratio of 1:1. (c) $I$–$V$ characteristics of ITO/PVP:Vulcan XC-72s/Al WORM memory devices in log–log scale.

the PVP:Vulcan XC-72s volume ratio too much such as more than 1:2 (by increasing the concentration of Vulcan XC-72s), an ohmic characteristics was observed with high current but without switching behavior. In particular, for the case of devices made with the PVP:Vulcan XC-72s

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volume ratio of 1:1, we observed the switching behavior for memory application. As shown the Figure 2(b), we first performed the 1st voltage sweep from 0 V to +5 V. An initial current level of the fabricated device was very low. Then, the current gradually increased to about ∼10 nA around a transition voltage (+3.3 V). And, then the current was abruptly increased near +3.3 V, indicating the transition of the device memory state from a high resistance state (HRS or OFF state) to a low resistance state (LRS or ON state), which is called the "SET" process. After the transition from HRS to LRS, the device was maintained at the LRS during the 2nd voltage sweep from 0 V to +5 V. Once we performed the set process (write), the memory devices were well maintained at the LRS for the 3rd and 4th sweeps from +5 V to −3 V and −3 V to 5 V, respectively. In other words, the devices can be turned from OFF to ON state and can remain as ON state, but can't be changed back to OFF state. These results demonstrate the typical characteristics of the WORM memory devices.

Our WORM memory devices exhibited the ON/OFF ratio as high as $\sim 10^6$ at the read voltage of 0.5 V.

Regarding on the mechanism of the memory operation, a filamentary conduction[23] or space charge limited current (SCLC)[24] have been proposed as the mechanism for charge transport in organic memory devices. Generally, the $I$–$V$ plot on the log–log scale has been analyzed to understand the underlying bistable switching mechanism in the memory devices.[25,26] Figure 2(c) shows a log–log plot of $I$–$V$ curve in the positive voltage sweep region for PVP:Vulcan XC-72s (1:1 ratio) WORM type memory devices. As shown in Figure 2(c), the fitting results for the HRS showed that the charge transport behavior is similar to a classical trap-controlled SCLC. More specifically, the $I$–$V$ is composed of three parts: the ohmic region ($I \propto V$), the Child's law region ($I \propto V^2$), and a region of steep current increase (slope of ∼8).[24] On the other hand, for the LRS case, the $I$–$V$ relation exhibited only an ohmic conduction behavior with slope of ∼1.1. This LRS is associated with the formation of conductive filaments within the composite layer during the "SET" process. Two types of filamentary conduction have been often reported for the polymer memory devices. One type is concerned with the carbon-rich filaments formed by local degradation of polymer films.[18] The other is related to the metallic filament formation from a local fusing, migrating of electrodes through the films.[27] In the LRS of the WORM devices in our study, we assume the mechanism of filaments formation resulting from pyrolysis of the polymer (PVP) and the sequent formation of conductive carbon-rich material (Vulcan XC-72s) surrounding the breakdown region.[28]

One of important properties of memory devices is memory retention time. We measured the retention performance of our WORM devices at room temperature, as

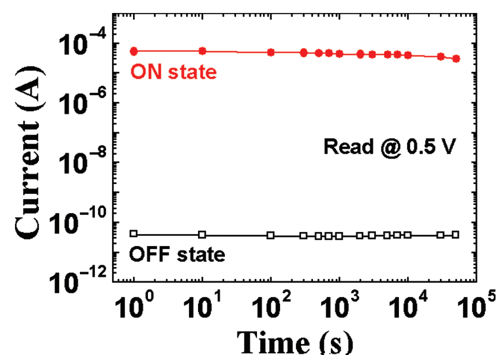


**Fig. 3.** Retention time characteristics of the two resistance states (ON and OFF states) measured at the read voltage of 0.5 V.

shown in Figure 3. Figure 3 shows the resistance values of two states (ON and OFF states) measured at the read voltage of 0.5 V. Relatively long retention time of $\sim 5 \times 10^4$ seconds was obtained for each state without any serious degradation, which demonstrates good memory performances of the mixture of PVP and Vulcan XC-72s. Note that a WORM type memory device has been demonstrated using an InP-ZnS nanoparticles embedded polymethyl methacrylate layer, independently with our study, which will attract more attention for particle-polymer composites non-volatile memory materials and devices.[29]

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## 4. CONCLUSIONS

We fabricated write-once-read-many times (WORM) type memory devices in 8 × 8 cross-bar array structure. Individual memory devices were fabricated as ITO/Poly(4-vinyphenol) (PVP):Vulcan XC-72s blends/Al structure. The fabricated memory devices exhibited the switching electrical characteristics from OFF to ON states, with a very high ON/OFF ratio ($I_{ON}/I_{OFF} \sim 10^6$) at the read voltage of 0.5 V. The retention characterization at room temperature showed a good retention performance of ∼50000 seconds without any serious degradation.

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