Direct observation of localized conduction pathways in photocross-linkable polymer memory

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Resistive switching in photocross-linkable polymer memory devices was found to occur in localized areas of the device. In order to elucidate the reason behind the switching, we used focused ion-beam to prepare a cross-section of the device. It was found that after the device was switched to the high conductive state, in certain parts of the device, the electrodes were only about 5 nm apart. This was probably caused by a combination of high electric field and metal injection into the polymer film. Gold injection into the polymer film by locally enhanced electric field was confirmed by transmission electron microscope-energy dispersive x-ray analysis. This model was in agreement with both the temperature dependent and transient behavior of our device. We conclude that the non-uniformities at the nanoscale interface of the electrode dominated the device characteristics while the polymer played only a secondary role. © 2009 American Institute of Physics.

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I. INTRODUCTION

Polymer memory devices are identified as one of the potential candidates for next generation memory storage.1,2 Ease of processing, flexibility,3,4 and stackability5–7 make it ideal for both complementary metal-oxide semiconductor integration and low cost applications. However, despite many years of development, the working mechanism is still highly debatable.8,9 Various mechanisms, e.g., field induced charge transfer,10–13 charge trapping,14–18 metal oxide switching,19,20 filament formation,21–24 and polymer conformation change25 have been proposed, but a comprehensive explanation with direct experimental proof has been elusive.

Cölle et al.19 and others26–29 have shown that the switching phenomenon occurred in localized areas of the polymer memory device. We have also observed similar effects in our stackable memory devices using a photocross-linkable polymer.7 Aluminum oxide switches,19 formation and rupture of carbon,23 metallic,24 or other filamentary channels22,30 have been suggested to explain the filamentary nature of switching for these polymeric devices. However, the precise nature of these filaments and the formation mechanism are still not clear. A similar mechanism was also proposed in resistive memory using inorganic film.21 To clarify the working mechanism, efforts have been made to directly observe the conducting filaments in these devices using electron microscopy.31,32 Due to its accessibility, filaments are more readily observed in a planar structure, although it does not necessarily represent the actual conditions in a vertical stack configuration. Filaments consisting of carbonaceous materials,33 silver dendrites,34 and other materials32,35 were observed in planar structures of devices over a wide range of materials. Filament formations have also been detected in vertical structures of chalcogenide36 and NiO37 devices.

Even though filament formation have been observed in various systems, the nature of the conductive pathways appeared to be very different in each system. Therefore, to fully understand the memory mechanism, it is important to find out how these filamentary pathways are formed in our polymer devices. Based on the results from thermal images of polymer devices in operation19,26 and the model of Dearnaley et al.,21 the conduction spots could range from 1 nm to 100 μm. Due to the small sizes and low density of these spots, it has been very difficult to observe these localized areas. In this paper, we describe a general method that can be used to study these highly conductive pathways.

We found that for our lithographically patterned devices using a photocross-linkable polymer, damages to the device appeared near the bottom electrode edge after many cycles of switching between high and low conductivity states.7 As the current density flowing through localized conductive spots can be very high, physical changes to the top electrode could be observed after switching. In order to exclude the effects of dust particles38 and other irregularities, the device area has to be made small enough so that the whole device can be examined at high magnification using a scanning electron microscope (SEM). Once the conductive spot is identified by the changes to the top electrode, a cross-section of the spot can be prepared by a focused-ion beam (FIB). Transmission electron microscope (TEM) can then be used to examine the local features which caused the switching.

II. EXPERIMENTAL

A. Device fabrication

4 × 4 μm² devices were fabricated using a photocross-linkable copolymer used previously.6,7 The chemical struc-
tecture of the polymer and device structure are shown in Figs. 1(a) and 2(a), respectively. The copolymer was synthesized by Suzuki polymerization of 9,9-bis(4-(6-(3-ethylxetan-3-yl) methoxy)hexyloxy)phenyl)-2,7-dibromofluorene, 9,9-bis(4′-diphenylaminophenyl)-2,7-dibromofluorene and 9,9-dioctylfluorene-2,7-bis(trimethylborate). The copolymer was then dissolved in 1,2 dichlorobenzene to form a 3 wt% solution. A photoacid generator (PAG), PAG203 (Ciba Specialty Chemicals) was added to the polymer solution in the weight ratio of 1:0.13 with respect to the copolymer.

A silicon wafer with 300 nm of thermally grown silicon dioxide was used as the substrate. The bottom electrode, consisting of 3 nm of chromium (as an adhesion layer) and 30 nm of gold, was patterned using standard lift-off techniques.

The polymer solution was then spin-coated onto the patterned electrodes and cured using a handheld UV lamp (wavelength 254 nm). The substrate was then annealed at 90 °C for 2 min and then 150 °C on a hotplate. The average polymer film thickness of the device, measured using a Dekkta 3030, was about 50 nm at the uniform region. After the curing process, the polymer became insoluble in organic solvent and was robust enough to withstand photolithography processes. Finally, the top electrode of aluminum (thickness 80 nm) was deposited and patterned using the lift-off method. All metal deposition was done by thermal evaporation in a vacuum chamber with base pressure of <10⁻⁵ Torr.

B. Electrical characterization

Electrical dc measurements were carried out in a Janis cryogenic vacuum probe station with a vacuum level of <10⁻³ Torr using an Agilent 4155C parameter analyzer. The aluminum electrode was biased as the reference electrode. Temperature dependence studies were conducted from 235 to 295 K. A larger temperature range was not possible due to the large difference in thermal expansion coefficient between the metallic and polymer films, causing the delamination of electrodes at lower temperatures. Transient current measurement was performed by applying a 500 μs pulse using the “stress force” function of the Agilent 4155C. The slow rising and falling time (about 100 μs) of the pulse was chosen to suppress the high transient charging and the discharging currents due to the capacitance of the device. The current of the device was measured using a high speed transimpedance amplifier, Femto DHPCA-100, connected to a Tektronix TDS3054 digital oscilloscope.

C. Preparation of device cross-section and TEM imaging

As mentioned earlier, high current density flowing through localized areas of the device could cause damage to the top electrode. However, in order to observe the nature of the filamentary conduction, it is important to limit the damage to the top electrode. For that reason, the polymer memory device under test was switched between high and low conductivity states for only five cycles by applying 4 and 10 V pulses alternatively. Finally, the device was switched to the high conductivity state (by applying a 4 V pulse), and transferred to a FEI Nova 600 Nanolab Dual-beam™ SEM/FIB for examination and cross-section preparation. Figure 2(b) shows the top view of the device where there was an irregular feature on the electrode. To protect the underlying layers from ion-beam damage, a carbon-rich platinum film was first deposited by decomposing a metal-organic precursor gas using electron beam. Ion-beam was then used to deposit a thicker layer of platinum. The cross-section of the area was cut out by FIB and transferred to a copper grid. The TEM study was performed using a JEOL 100CX and a FEI Titan at accelerating voltages 100 and 300 kV, respectively.
III. RESULTS AND DISCUSSION

The device was first “formed” by increasing the voltage until the current reached the compliance current of 10 μA. After the device was formed, when the voltage bias was swept from 0 to 10 V, the device switched from a low conductivity state (off state) to high conductivity state (on) at around 3.5 V and exhibited a negative differential resistance (NDR) behavior at higher voltages [Fig. 1(b)]. It remained in the high conductivity state when the voltage was swept back to 0 V. The device could be switched back to the low conductivity state by applying a 10 V pulse to it. Similarly, it could be switched to the high conductivity state by a 4 V pulse. It is important to note here that devices with switching characteristics can also be fabricated without PAG using shadow masked electrodes. This proved that the memory phenomenon was not due to the addition of the PAG.

To find the cause of the high conductivity state, we examined the area where high density of current flowed through. Figures 2(c) and 2(d) show the TEM images of the cross-section of the area with irregularities. Close to the edge of the gold electrode, the bottom and top electrodes were almost in contact with each other. The closest distance between the two electrodes was about 5 nm, while the average distance in the uniform area was about 50 nm. Due to the close proximity and the sharp edges of the two electrodes, very high electric field could be generated between the electrode tips. The electric field at the tip was estimated to be about ten times more than that at the uniform regions even without considering the local field enhancement due to the sharp tip. Therefore, most of the current would flow through these localized spots even when a small voltage is applied to the device, which is consistent with earlier observations.  

This result, however, does not exclude the possibility of the formation of metallic bridges in our device. When the voltage bias was further increased, the current density flowing through these local spots could become so large that the highly conductive paths were damaged by joule heating. This explains how the device was switched from the high to low conductivity state.

Next, we consider how these conductive spots are produced. We observed, from the TEM images, that the gold electrode was not uniform throughout the device. The electrode was flat in the center, but was irregular near the edges. This was due to the lift-off process that we used to pattern the electrode. Figures 3(a) and 3(b) shows the scanning TEM (STEM) images of two such regions after the device was formed. We examined the differences between these two sections using TEM-energy dispersive x-ray spectroscopy (TEM-EDS). Figure 3(c) shows the line scan data of the gold Lα signal. The results show that more gold was drifted deeper into the polymer at places where the shape of the electrode was not regular. This could be explained by the much higher electric field at such locations.

During the forming process, gold ions were drifted into the polymer film by the electrical field generated between the two electrodes. At certain places where the electric field was enhanced due to the nonuniformity of the electrode, more gold ions were drifted deeper into the polymer film. The local conductivity of the polymer was thus increased by the influx of gold ions. The combination of higher electric field and increased conductivity resulted in very high current density at the local area. The forming process was stopped when the current of the device reached the compliance current.

Subsequently, when a high enough voltage bias was applied to the device, local current density at these spots can reach very high values due to the combination of enhanced electrical field and high local conductivity. Local deformation may occur as a result of the joule heating and high electric field, giving rise to the structures in Figs. 2(b) and 2(c). As mentioned earlier, these local conductive spots may be destroyed when an even higher voltage is applied to the device. New conductive spots could then be formed from the irregular structures surrounding the damaged area.

Next, temperature dependence study of the high and low conductivity states of the device was performed. Figure 4 showed the Arrhenius plot of the current at the on and off states of the device. At the on state, the current showed a very weak dependence on temperature ($E_a$ activation energy $\sim 24$ meV), indicating possibly a metallic or tunneling conduction mechanism. On the other hand, when the device was at the off state, the current showed a much larger temperature dependence ($E_a - 0.57$ eV), implying that a thermally acti-
vated mechanism was active. This could probably be related to the transportation of charges through semiconducting polymer. A more detailed study on the conduction mechanism was complicated by the nonuniformity of the device. Nevertheless, these results are consistent with our model of formation and destruction of conductive pathways.

Transient current measurements were performed on the devices to observe the switching behavior when an electrical pulse was applied to the device. Figures 5(a) and 5(b) show the typical transient behaviors when a writing pulse (4 V) and an erasing pulse (10 V) were applied to the device. During the writing process, there were short durations when the current dropped below a certain level, possibly indicating the annihilation of weak filamentary paths. The current level was restored when new pathways were formed by the electric field. On the other hand, current spikes were observed during the erasing pulse. This could be explained by the formation and rapid destruction of the conductive pathways. Even though conductive spots could be formed by the high electric field during the erasing process, these pathways were not stable under the high voltage and could be easily destroyed by the large current density they needed to pass through. This explains the relative instability of the $I-V$ curve in the NDR region, where there is a competition between formation and destruction of weaker filaments. These transient measurements provided additional information on the switching dynamics of conductive pathways during the writing and erasing processes of the device.

In conclusion, we have described a FIB cross-sectioning method to directly observe local conductive spots in our polymer memory device. Based on the TEM results, we conclude that the memory mechanism is due to the formation and annihilation of filaments. We also proposed a model to describe the formation of these highly conductive pathways with evidences from STEM-EDS. During the forming process, metal ions are injected into the polymer film by enhanced localized electric field. When a sufficiently high voltage bias is applied to the formed device, highly conductive spots are created by the locally enhanced electric field and high current density. These conductive spots are destroyed by joule heating when a higher voltage is applied to the device. Temperature dependence studies were performed on the device and the results were consistent with our model. Transient current measurement further enhanced our understanding on the switching dynamics of the device.

We have shown that nonuniformities in the device, either intentionally or unintentionally introduced during the fabrication process, are capable of dominating device characteristics. The polymer in our device played only a secondary role in the switching mechanism. There are several reports in the literature describing polymer memories with similar device characteristics but explained by different mechanisms. While it is difficult to generalize our findings to all material systems, we believe that it is necessary to carefully examine the nonuniformities in both the electrode and film when studying the device mechanism.

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