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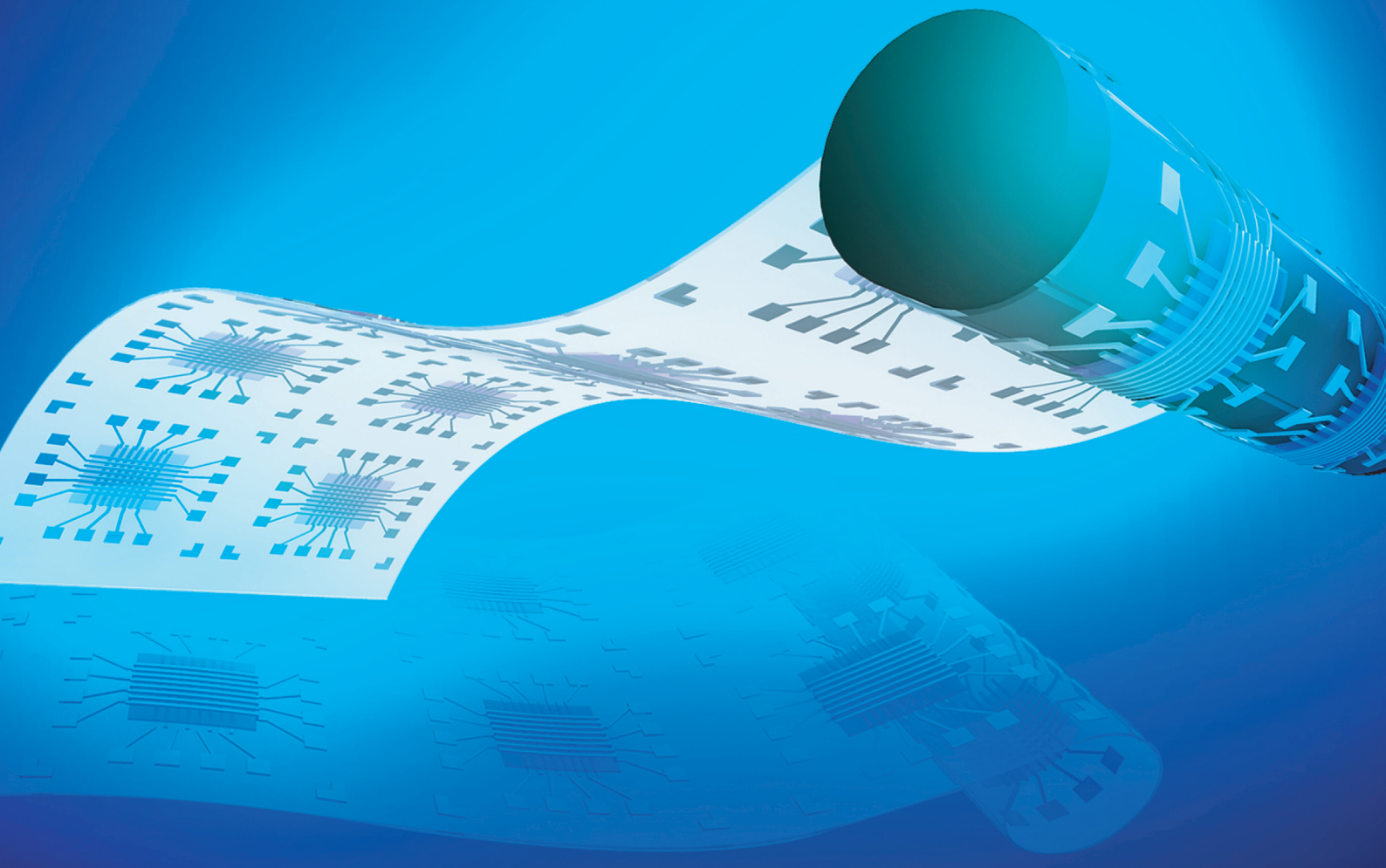

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Flexible Memory Devices

Stable Switching Characteristics of Organic Nonvolatile Memory on a Bent Flexible Substrate

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Organic-based electronics have received great attention due to their material variety and advantageous properties such as flexibility, printability, and light-weightness.[1,2] Their low costs, based on their ease of fabrication and large-area processing capabilities, increase the merits of organic electronics even more.[3,4] Consequently, organic electronics, including organic solar cells, light-emitting diodes, thin-film transistors, and memories, have been extensively investigated for the realization of practical device applications.[5–8] Among these, organic memories have emerged as an excellent candidate for the next-generation information storage media because of their potential application in flexible memory devices.[8–18] There are different types of organic memories. They are distinguished as ferroelectric,[13,14,18] flash,[15,18] and resistive-type organic memories[16–18] in terms of the operating mechanisms and device structures. Each type of organic memory has its own advantages and disadvantages, which has been discussed in a recent review article.[18] In general, the ferroelectric and flash-type organic memories operate in a relatively high voltage range, whereas the resistive-type organic memory requires lower operating voltages. Furthermore, the device structure can be simpler in resistive-type memory.[18]

Flexibility is particularly important for future electronic applications such as foldable and wearable electronics. Much research has been done to apply the flexible electronics technology to practical device areas such as solar cells, thin-film transistors, photodiodes, light-emitting diodes, and displays.[19–23] The research on flexible memory was also initiated for these future electronics applications. In particular, organic-based flexible memories have merits such as a simple, low-temperature, and low-cost manufacturing process. Several fabrication results of organic resistive memory devices on flexible substrates have been reported.[24–26] These studies so far have focused on manifesting the resistive switching characteristics on flexible substrates and have reserved the detailed investigations of the switching characteristics of organic memories under bending conditions. For better understanding of the performance of flexible memory devices and for the realization of practical flexible memory devices, more complete device parameters (ON/OFF ratio, threshold voltage, endurance, and retention time) as a function of the degree of bending need to be characterized and compared.

In this work, we report our detailed study results of the switching characteristic of an organic memory on a flexible substrate that was bent to various degrees. A composite of polyimide (PI) and 6-phenyl-C61 butyric acid methyl ester (PCBM) was used as the active material of our resistive memory. PI has thermal stability, good chemical resistance, and excellent mechanical properties, and it has been used as insulating and mechanical-support material in electronics industries for a long time.[23,27,28] On the other hand, 6-phenyl-C61 butyric acid methyl ester (PCBM) has been used as electron acceptor in organic heterojunction solar cells.[29,30] Subsequently, PI and PCBM composite materials have been used as the active materials of organic non-volatile memory, and they have shown mechanical robustness and good thermal stability.[31] We fabricated PI:PCBM organic memory devices on poly(ethylene terephthalate) (PET) flexible substrates. Various device parameters were characterized according to the degree of bending. We found that the threshold voltage and ON/OFF ratio remained nearly constant regardless of the degree of bending, indicating the stability of the electrical characteristics of our memory devices with bending stress. Moreover, reliable memory performances in terms of endurance cycles and retention time were demonstrated regardless of bending circumstances.

The memory device fabricated in this study is illustrated in **Figure 1**. Figure 1a is the schematic of a 8 × 8 cross-bar array-type organic memory device on a bent substrate. The details of the device fabrication are explained in the Experimental section and the Supporting Information. Figure 1b shows a photographic image of a fabricated memory device in a bent condition. The degree of bending was expressed by the radius of curvature (r) and also the distance (d) between two end points of the arc, as indicated in the figure.[32–34] The distance was measured using digital vernier callipers. The radius of the curvature was determined from the distance (see Figure S2 in the Supporting Information). Figure 1c illustrates the schematic cross-sectional view of the structure of the Ti/Au/Al/PI:PCBM/Al layered memory cell on the PET substrate. We used the Ti/Au bilayer (Ti as an adhesion layer and Au as a buffer layer) to reduce the oxidation of the bottom Al electrode caused by the PET substrate material. It has been reported that oxygen elements from the plastic substrate can oxidize the bottom metal electrode during metal deposition and thus may affect the

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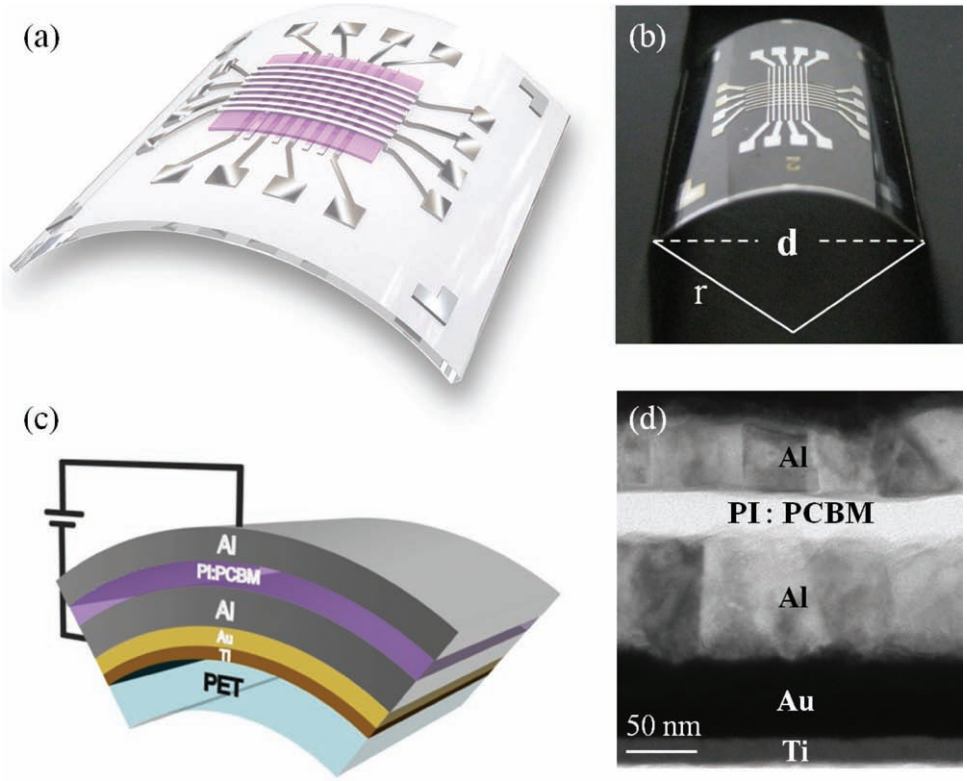

Figure 1. (a) Illustrated and (b) optical images of the 8 × 8 array-type Ti/Au/Al/PI:PCBM/Al flexible organic memory devices. (c) Schematic view of a Ti/Au/Al/PI:PCBM/Al memory cell. (d) Cross-sectional TEM image of the layers in a memory cell.

electrical characteristics of the memory.[35] Figure 1d shows the cross-sectional transmission electron microscopy (TEM) image of a memory cell fabricated in this study. Good structural properties were observed in the TEM study: no agglomerations of PCBM were observed in this figure, indicating the uniform dispersion of PCBM in PI. Also, the energy dispersive x-ray spectroscopy (EDX) analysis results verified the reduction of the oxygen contents within the bottom Al electrodes with the use of the Au buffer layer, as compared with the ones without the Au buffer layer (see Figure S4 in the Supporting Information). Furthermore, the element Au was absent within the organic active layer; unintentional penetration of Au metal could create filamentary paths and short out the memory cell (see Figure S3 in the Supporting Information for the EDX image). The carbon element was mainly detected in the organic active layer. From these analysis results, it can be concluded that the resistive switching of our memory device is mainly functioning in the PI:PCBM active layer.

As with the results of good structural formation, our memory devices showed well-defined memory-switching characteristics. The current-voltage (I-V) switching characteristic of a memory device is shown in **Figure 2**. The initial state of the memory device was a high-resistance state (OFF state). When the applied bias exceeded 3.5 V, the OFF state of the device was turned into a low-resistance state (ON state). After that, when the voltage was decreased back to 0 V, the ON state remained, showing a non-volatile memory behaviour. To turn off the device, the applied voltage was swept from 0 to 8 V; the device tracked the previous current characteristics of the ON state, and then the device was turned off after 5 V, showing a negative differential resistance (NDR) region. The switching characteristics in Figure 2 are so-called unipolar-type. The unipolar switching is achieved by successive application of voltages with the same polarity.[36] And, these resistive switching characteristics can be explained by

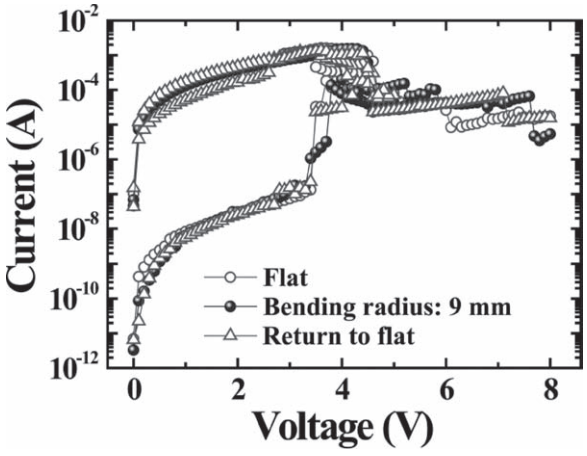

Figure 2. I-V characteristics of a flexible organic memory device. The open circles show the I-V curve when the device was flat, the filled circles show when the device was bent the most (9 mm bending radius condition), and the open triangles show when the device returned to the flat condition after bending.

the charge-trapping mechanism proposed by Simmons and Verderber[37] and Bozano et al.[38,39] To verify if our memory device can show the reliable switching characteristics even under bent conditions, we performed the I-V measurements under various degrees of bending. In the bending test, 9 mm was the minimum radius of curvature (i.e., the maximum bending condition) used in our study (when we bent more than this, we often observed irreversible failure of the memory devices). The memory exhibited almost the same switching characteristics in both the flat and the maximum bending conditions, as shown in Figure 2. To validate the reversibility of the electrical properties of the flexible memory device, we measured the electrical characteristics after the device was returned to the original flat condition after the bending. The switching characteristics did not change significantly after the bending (Figure 2), indicating the resilience of the electrical property of our memory device with the bending stress. The ON/OFF current ratios were over 10^4 in all three cases: flat, maximum bending, and returned-flat conditions (see Figure S5 in the Supporting Information for the entire I-V characteristics with different bending conditions.).

The observed stability of the electrical characteristics under the bending condition is one of the key requirements for the practicality of flexible memory devices. This required property of our memory device was studied in more detail. We investigated the ON/OFF ratio as a function of the degree of bending. As shown in **Figure 3a**, the ON/OFF ratios of the memory device remained over 10^4 even when bending was increased. Also, the deviations of the ON/OFF ratios were insignificant at all the bending conditions shown in the plot. In addition, the stability of the memory performance during repetitive bending conditions is also a critical factor for realizing practical flexible memory devices. To test this, the ON/OFF ratios were monitored with increasing bending cycles, as shown in Figure 3b. The ON/OFF ratios were measured when the device was at the maximum bending condition (bending radius of 9 mm). Our device retained the high ON/OFF ratio of over 10^4 without any significant electrical degradation during the 140-cycle test. The error bars in Figure 3 and 4 are the standard deviations from the measurements on several memory devices (~20 memory devices).

There are other parameters that need to be monitored to ensure a stable memory performance under flexible conditions. In particular, the distributions of the threshold voltages (the set and the reset threshold voltages) should be investigated to characterize the complete memory operation. If the set and the reset threshold voltages overlap, then the memory switching (turn-on and turn-off) cannot be controlled precisely, causing a serious electrical malfunction. In this regard, we monitored the distribution of the set and the reset threshold voltages according to the bending radius. As shown in **Figure 4a**, there was no overlap observed between the set and the reset threshold voltages within the range of bending conditions, indicating the good stability of our memory devices under bending. The retention characteristics of the information states are also an important property for the memory devices. We measured the retention times of our memory device in both the flat and the maximum bending conditions (bending radius of 9 mm). As shown in Figure 4b, our device showed long retention times during 10^4 seconds in both the flat and the maximum bending conditions. No serious degradation was exhibited, even in the bending condition. Note that the actual retention time of the device can be much longer than 10^4 s, indicating a reasonably stable behavior in terms of information storage capability. Additionally, the endurance property of the flexible memory device was investigated. The current fluctuations for both the ON and OFF states need to be small during the endurance test, as is required for a reliable memory device. Figure 4c,d show the endurance characteristics of the device in the flat and in the maximum bending condition. The endurance property under bending was good, showing few current fluctuations in the ON and OFF states. The data shown in Figures 4c,d indicate the stable endurance characteristics of our memory device in both the flat and bending conditions.

In conclusion, we fabricated organic, non-volatile memory devices on flexible substrates using PI:PCBM composite as an active layer. The flexible memory devices showed successful rewritable switching properties under the bending circumstances. There were no significant deviations in the ON/OFF ratios regardless of the degree of bending or the number of bending cycles. Furthermore, our flexible memory device exhibited a long retention time and stable endurance under the bending conditions, demonstrating promising characteristics for application to future flexible memory devices.

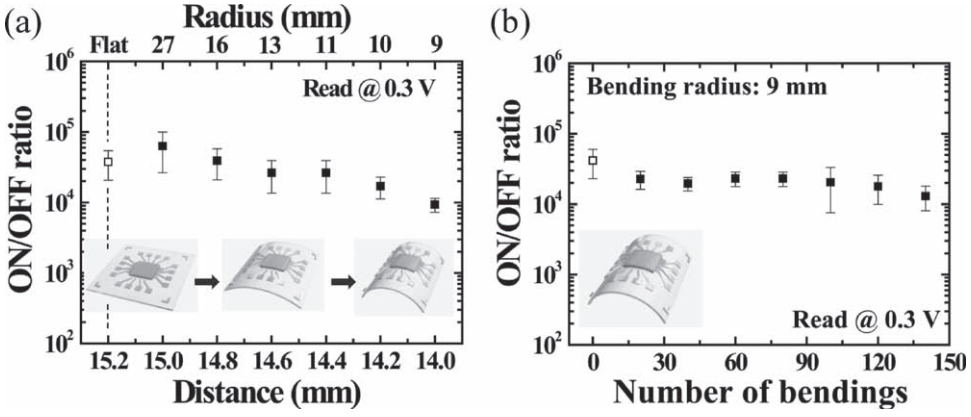

Figure 3. (a) ON/OFF ratio as a function of the bending condition (the substrate distance and the bending radius). (b) ON/OFF ratio as a function of the number of bendings.

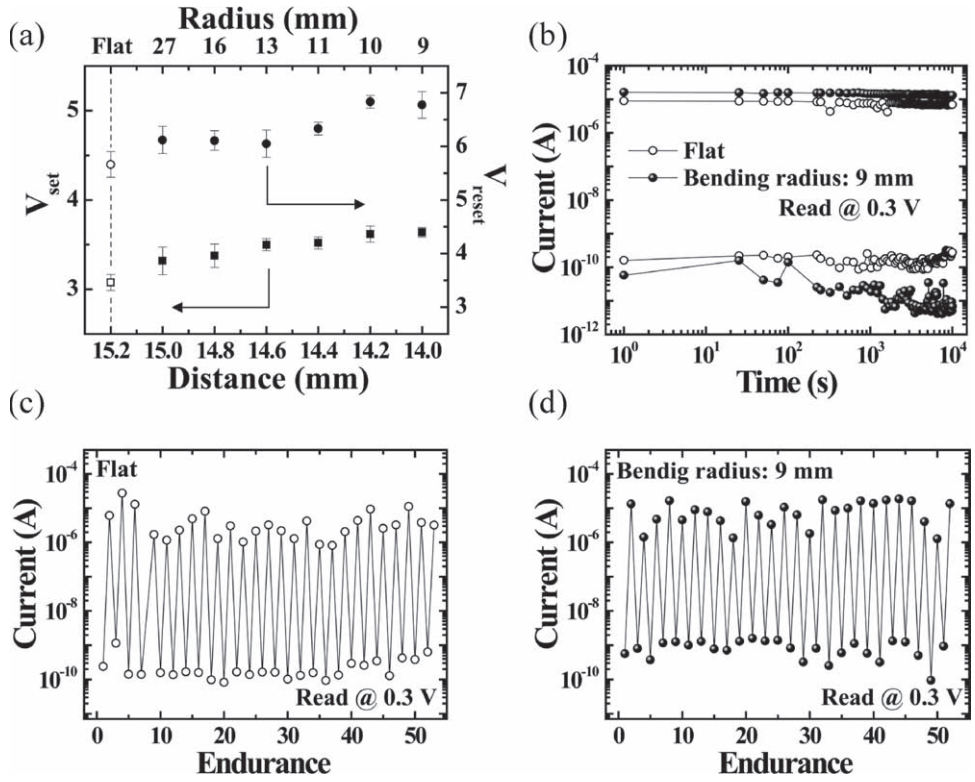

Figure 4. (a) V_{set} and V_{reset} threshold voltages as a function of the bending condition (the substrate distance and the bending radius). (b) Retention times of the memory information when in the flat and in the bent condition. Endurance cycles when the memory device was flat (c) and bent (d).

Experimental Section

To make flexible organic memory devices on a PET substrate, the PET substrate was first cleaned by the typical ultrasonic cleaning process using acetone, methanol, and de-ionized water for three minutes, in this order. The bottom electrodes were deposited with eight lines of a 100 μm line-width pattern using a shadow mask by an electron beam evaporator with the deposition rate of 0.3 Å/sec at a pressure of ~10^{-7} torr. The deposited metal consisted of Ti (10 nm)/Au (30 nm)/Al (70 nm). To prepare an active layer for the organic resistive memory, we used biphenyltetracarboxylic acid dianhydride p-phenylene diamine (BPDA-PPD) as a PI precursor; the BPDA-PPD was dissolved in N-methyl-2-pyrrolidone (NMP) solvent (BPDA-PPD:NMP solvent = 1:3 weight ratio). The 6-phenyl-C61 butyric acid methyl ester (PCBM) was dissolved in NMP solvent at a concentration of 0.5 wt%. Then, a PI:PCBM composite solution was prepared by mixing the PI solution (2 ml) with the PCBM solution (0.5 ml). The Al surface on the PET substrate was exposed to UV-ozone treatment for 10 min to improve the reliability of the organic resistive memory.[40] Then, the PI:PCBM composite solution was spin-coated onto the Al electrodes/PET substrate at 500 rpm for 5 sec and subsequently at 2000 rpm for 35 sec. The coated film was soft-baked at 60°C on a hotplate for 10 min in a N_2-filled glove box to dry and harden the deposited organic active layer. After the baking, the bottom electrode pads were exposed by rubbing with a methanol–soaked swab for the electrical probing. Next, we hard-baked the memory devices in a vacuum oven at 100°C for 24 hours to enhance the film uniformity and for the evaporation of the residual solvent and thermal curing. The thickness of the PI:PCBM composite active layer was measured from the TEM analysis to be ~30 nm. Finally, we deposited the top electrodes with a thickness of 50 nm, crosswise to the bottom electrodes. All electrical measurements were conducted using a semiconductor characterization system (Model 4200-SCS, Keithley, Inc.) at room temperature in a N_2-filled glove box (see Figure S1 in the Supporting Information for more details on the memory device fabrication.).

Supporting Information

Supporting Information is available online from Wiley InterScience or from the authors.

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