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Twistable nonvolatile organic resistive memory devices

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ABSTRACT

We fabricated an 8 × 8 cross-bar array-type organic nonvolatile memory devices on twistable poly(ethylene terephthalate) (PET) substrate. A composite of polyimide (PI) and 6-phenyl-C61 butyric acid methyl ester (PCBM) was used as the active material for the memory devices. The organic memory devices showed a high ON/OFF current ratio, reproducibility with good endurance cycle, and stability with long retention time over 5×10^4 s on the flat substrate. The device performance remained well under the twisted condition with a twist angle up to ~30°. The twistable organic memory device has a potential to be utilized in more complex flexible organic device configurations.

1. Introduction

Numerous studies have reported on organic-based electronic devices such as organic light-emitting diodes, transistors, photovoltaics, and nonvolatile memories since the discovery of conducting polymers [1–5]. These organic-based materials and devices have many merits due to their innovative potential for flexibility and their easy and low-cost large-scale fabrication achieved by spin-coating and roll-to-roll processes [3,6–17]. In particular, organic nonvolatile memory (ONVM) devices are being widely investigated for next-generation data storage applications [15,17–23]. Although ONVMs still require considerable development to enhance device performances in comparison to inorganic nonvolatile memory devices, recent reports on the flexibility of organic memory and other types of devices have demonstrated various possibilities in unconventional device applications [24–27]. In future electronics, flexibility will be a very important factor in the development and applications of foldable and wearable electronics. Many research groups have reported amazing results for active materials, electrodes, and integrated circuits in flexible electronics based on organic and inorganic materials [26,28–31]. In addition, our group recently reported on molecular-scale flexible electronics achieved using self-assembled monolayers [32].

Likewise, ONVMs will be important in flexible electronic device applications. There are multiple types of ONVMs, which are classified as ferroelectric [17,22,23], flash [15,23], and resistive type [23,33,34] organic memory devices based on their operating mechanisms and device structures [23]. Among these types, resistive type memory devices have advantages such as lower operating voltages and simpler device structures. We recently reviewed some of the existing organic resistive memory devices in terms of performance enhancement and architectural issues, including the one transistor–one resistor (1T–1R)-type memory, the one diode–one resistor (1D–1R)-type memory, three-dimensionally integrated memory, and flexible memory [24,25,33–36]. Until now, most reports on flexible

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memory devices have focused on bending conditions. However, such devices should be flexible in a variety of mechanically deformed configurations. For example, flexible devices should be not only bendable but also twistable or stretchable if possible. Thin and wavy Si-based foldable or stretchable electronic devices that are embedded in or deposited on poly(dimethylsiloxane) (PDMS) have been widely reported for various mechanical modification conditions [28,31,37].

In this work, we report the results of a study on the switching characteristics of organic resistive memory devices on a flexible substrate that was twisted 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, as in our previous studies [24,34,35]. PI and PCBM composite materials have shown chemical and mechanical robustness and good thermal stability [35]. We fabricated PI:PCBM organic memory devices on flexible and twistable poly(ethylene terephthalate) (PET) substrates. The device parameters were characterized according to the degree of twisting, up to a twist angle of approximately 30°. We found that the statistical threshold voltage distribution and the ON/OFF current level remained well regardless of the degree of twisting, indicating the stability of the electrical characteristics of our memory devices under twisting stress. Moreover, reliable memory performance in terms of endurance cycles and retention time was demonstrated under twisting conditions.

2. Experimental section

To produce twistable organic memory devices on a PET substrate, the PET substrate was first cleaned by the typical ultrasonic cleaning process using acetone and IPA for 5 min, respectively. The bottom electrodes were deposited with eight lines of a 100-μm line-width pattern using a shadow mask by a thermal evaporator with the deposition rate of 5 Å/s at a pressure of $\sim 10^{-7}$ torr (Fig. 1a). The deposited metal consisted of Al (70 nm thickness) and the surface of the Al bottom electrodes was exposed to UV–ozone treatment for 10 min. Note that the surface of the Al bottom electrodes may contain the native Al oxide layer. The thin Al oxide layer may enhance the reliability of the organic resistive memory devices [38,39]. 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) and the PI:PCBM composite solution was spin-coated onto the Al electrodes/PET substrate at 500 rpm for 5 s and subsequently at 2000 rpm for 35 s (Fig. 1b). 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 step, the bottom electrode pads were exposed by rubbing with a methanol-soaked swab for electrical probing (Fig. 1c). Next, we hard-baked the memory devices in a vacuum oven at 110 °C for 24 h to enhance the film uniformity, evaporate the residual solvent, and perform thermal curing. The thickness of the PI:PCBM composite active layer was measured at ~60 nm by transmission electron microscopy (TEM) analysis. Finally, we deposited the top electrodes at a thickness of 70 nm crosswise to the bottom electrodes (Fig. 1d). Fig. 1f shows a photographic image of the completely fabricated our twistable organic memory devices.

Fig. 2a shows a cross-sectional TEM image of an organic memory cell. Good structural properties were observed by TEM; no agglomerations of the PCBM were observed in this image, indicating a good dispersion of the PCBM in the PI. Furthermore, aluminum was found to be absent in the organic active layer by the energy dispersive X-ray spectroscopy (EDS) data (Fig. 2b). The accidental penetration of Al elements would create filamentary paths and short out the memory cell. Carbon elements were mainly detected

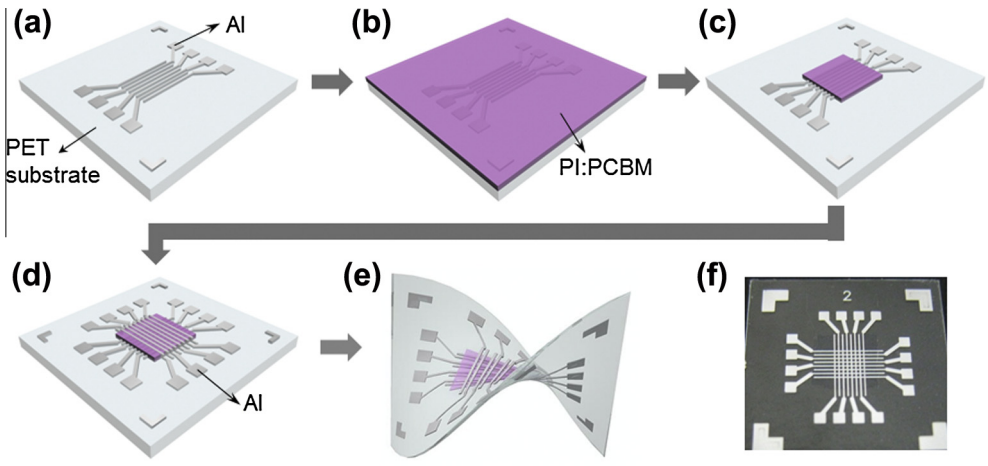

Fig. 1. (a–d) The fabrication process of the Al/PI:PCBM/Al organic resistive memory devices in an 8 × 8 array structure on a PET substrate. (e) Schematic illustration of twisted organic resistive memory devices. (f) A photographic image of the fabricated organic memory devices under the flat condition.