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Tuning the electrical switching of polymer/fullerene nanocomposite thin film devices by control of morphology

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The working principles of thin film organic memory devices remain debated and tunability has been less presented. We show that the nanostructure of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and polystyrene (PS) allows facile tuning of switching behavior for low PCBM concentrations upon annealing above the glass transition temperature of PS. By increasing the PCBM concentration from 2 to 6 wt %, the switching voltage from off to on state during the first voltage sweep systematically decreases. In subsequent voltage sweeps negative differential resistance effect is observed. Above ca. 7 wt %, chains of PCBM clusters couple the electrodes, which leads to Ohmic behavior. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3033221]

Various kinds of memory and switching devices have been reported recently based on different electroactive organic layers sandwiched between two metal electrodes where the current increases by several orders of magnitude above a certain threshold voltage V_{th} or where negative differential resistance (NDR) is observed.[1] However, the research has mainly focused on rapid search for new materials and device concepts, whereas less emphasis has been put toward understanding of the effect of materials properties and morphology on the device function or to tune the switching and NDR. Furthermore, the underlying science is still in progress, as no coherent theoretical understanding has so far been presented to explain the results except for one phenomenological model[2] even if electric-field-induced charge transfer,[3] Coulomb blockade,[4] and filamentary conduction[5] have been proposed as the working mechanism. Verbakel *et al.*[6] reported that the resistive switching in two terminal organic nonvolatile memories could be solely due to the breakdown of a native oxide layer at the aluminum electrode interface. Accordingly, the organic semiconducting layer would only act as a current limiting series resistance.

In this report a single layer organic thin film device, allowing tuning of switching and NDR, is constructed by sandwiching a nanocomposite of fullerene-derivative [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) and polystyrene (PS) between two aluminum electrodes. To explore the connection between the device behavior and the underlying morphology and to tailor the active material composition, we present a systematic study of the morphology by using transmission electron microscopy (TEM) specifically in the cross-sectional direction in relation to the devices. This is relevant for fullerene-based memories, but we foresee a broader significance toward generic nanocomposite memories to understand their working concepts and tunability, which have remained poorly understood.

PCBM/PS thin films were spin coated onto NaCl substrates (Sigma–Aldrich, IR crystal window) from a ternary mixture of analytical grade chloroform, PS (Aldrich, 50:50 mixture of two molecular weight components, namely, M_w =4000 g/mol and M_w=200000 g/mol), and PCBM (Nano-C, Inc.). The concentration of chloroform in each PCBM/PS composition was kept constant to ensure comparable film thicknesses. After spin coating, the films were annealed at 120 °C for 90 min under a vacuum of 1×10^{-3} mbar and were thereafter floated off from the substrate onto de-ionized water and collected onto TEM grids for plan-view TEM (FEI Tecnai 12). To understand the electrical behavior in thin film devices, it is relevant to study not only the plan view but also the cross-sectional morphology as the interfaces can have an effect on the morphology. Details of sample preparation for cross-sectional TEM have been given elsewhere.[7,8] Figs. 1(a)–1(d) show the cross sections of the PCBM/PS thin films where large fraction of the clusters appears to form close to the air/film interface. Clusters can also penetrate through the film interface and, in addition, hemispherical clusters form close to the film/substrate interface having the flat surface toward the substrate inter-

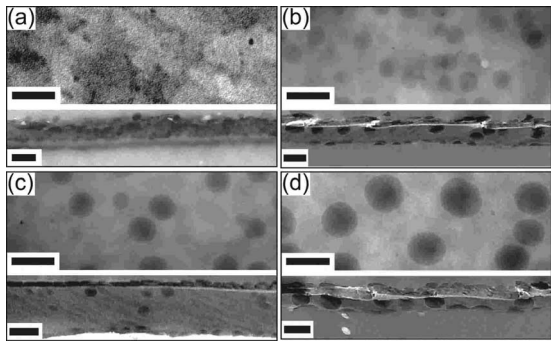

FIG. 1. TEM micrographs showing the plan view (top) and cross-sectional view (bottom) for 120 °C annealed (a) 5 wt %, (b) 10 wt %, (c) 20 wt %, and (d) 40 wt % PCBM/PS thin films. The top interfaces in the cross sections are air/film and the bottom film/substrate interfaces. All scale bars are 200 nm.

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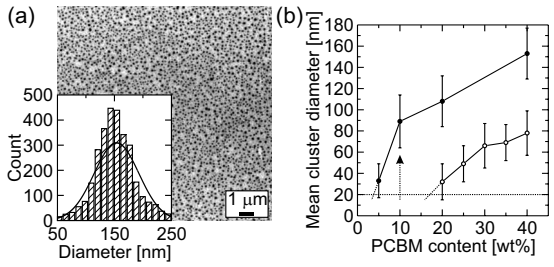

FIG. 2. (a) Size distribution for 120 °C annealed 40 wt % PCBM/PS. (b) Mean cluster diameters in PCBM/PS thin films before (open symbols) and after thermal annealing at 120 °C (closed symbols) as determined from the TEM micrographs. The error bars indicate the standard deviation and the smallest detectable particle size is ca. 20 nm.

face. Note also that the clusters can be quite large in comparison to the film thickness: chains of clusters [Fig. 1(b)] or single large clusters [Fig. 1(d)] can extend from one interface to the other.

Image processing (ImageJ) and data analysis (Matlab) were employed on the plan-view TEM micrographs to determine the cluster size distributions of PCBM. Figure 2(b) shows mean cluster diameters together with the associated standard deviations for each PCBM/PS composition before and after thermal annealing at 120 °C. Annealing and higher PCBM concentrations inevitably lead to increase in cluster size. This growth is most evident in the 10 wt % composition: prior to annealing aggregation is not observable at the resolution of TEM, whereas annealing at 120 °C leads to appearance of clusters of roughly 90 nm in diameter. An important indirect conclusion can be drawn: that there are larger clusters grown throughout the thin films due to annealing would be difficult to explain, unless there were PCBM moieties finely dispersed throughout the nonannealed thin films even if not resolved in TEM. In other words, around the observable PCBM clusters there exists a continuous matrix of finely dispersed PCBM that is responsible for the formation and growth of the observable clusters.

Next we discuss the electrical characteristics in devices where PCBM/PS has been sandwiched between two parallel aluminum electrodes. The devices were fabricated as reported previously[7] except that annealing was performed at 120 °C, i.e., above the glass transition temperature of PS ($T_{g,\mathrm{PS}} \approx 100$ °C). Without added PCBM, only small leakage current is observed without any switching or NDR [Fig. 3(a)]. By contrast, for 2 wt % of PCBM, switching of the current density by 6–7 orders of magnitude from the initial low current off state to high current on state takes place at ca. 9 V in the first voltage sweep, followed by NDR in the subsequent voltage sweeps [Fig. 3(a)]. Increased PCBM concentrations up to 5 wt % allow to tune the switching voltage from ca. 9 to 4 V [Figs. 3(a) and 3(b)]. We suggest that this is due to the shorter average PCBM separation due to increased concentration. Above ca. 7 wt % [Fig. 3(c)] Ohmic *I-V* curves are observed instead of switching or NDR, starting from the first voltage sweep at voltages as low as 1 mV, indicating that the device is short circuited. Based on the morphology study, the PCBM clusters can now form electrically connected chains of clusters [Figs. 1(b)–1(d)] from one electrode to the other and thus short circuit the aluminum electrodes.

To explain the switching behavior below 6 wt %, we next propose a model based on the device characteristics and the underlying device morphology. Let us model the aggregated PCBM/PS system with two homogeneous dielectric spheres ($\epsilon_{\mathrm{PCBM}}=3.9$, Ref. 9) that are placed into another dielectric medium ($\epsilon_{\mathrm{PS}}=2.6$) and subjected to a uniform and constant electric field (E_0). The electric field in the system can be evaluated by using the approach of Goyette and Navon,[10] and the result is shown in Fig. 3(d), which indicates that the polarization of the PCBM clusters can lead to a local increase in the electric field between adjacent clusters. Although the origin of V_{th} might be explained by the previously presented model that assumes the presence of a thin insulating oxide layer at the semiconductor/metal interface,[6] that model is unable to explain the presently observed shift in V_{th}

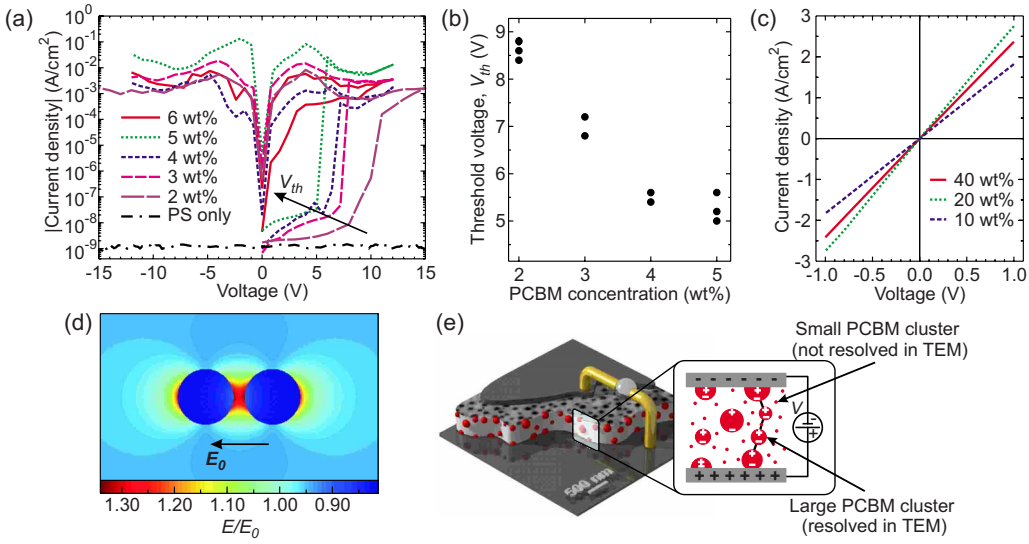

FIG. 3. (Color online) (a) Absolute current density as a function of voltage for pure PS, thickness $d=200$ nm, and 2–6 wt % PCBM/PS compositions ($d=250-260$ nm). (b) V_{th} as a function of PCBM concentration. (c) Current density as a function of voltage for 10–40 wt % PCBM/PS compositions ($d=250$ nm), showing Ohmic behavior. (d) Strength of the electric field in the vicinity of two dielectric spheres where an initially uniform electric field (E_0) is applied. (e) Combination of a TEM micrograph and a schematic illustration showing the polarization between the PCBM clusters separated by the PS matrix. All devices were annealed at 120 °C.

[in Fig. 3(a)] and absence of switching for 0 wt % [Fig. 3(a)] and >7 wt % [Fig. 3(c)]. However, the polarization of the PCBM clusters and generation of a stronger electric field between adjacent clusters along the direction of the electric field could account for these effects as schematically shown in Fig. 3(e).

We suggest that the NDR is an outcome of the tunneling process between the PCBM clusters. The NDR is similar to what has been observed in "electroformed" devices by Simmons and Verderber[11] and later by Thurstans and Oxley,[12] where inclusion of metal into the dielectric or semiconductor material under the influence of electric field has been clarified as the reason for this phenomenon. Since we have previously shown the absence of metal inclusion in our PCBM/PS devices,[7,8] the PCBM clusters in the PS matrix must act as the "formed" islands and give rise to the NDR.

In conclusion, the electrical behavior of the devices falls into three different categories. (*i) Switching from a high resistance state to a low resistance state at* V_{th} *in the first voltage sweep*. The position of V_{th} could be tuned by varying the PCBM concentration. V_{th} was suggested to result from the polarization of the PCBM clusters and generation of a stronger electric field between adjacent clusters. *(ii) NDR in subsequent repeated voltage cycles.* The NDR can be associated to similar effects observed in electroformed devices with the added advantage that the PCBM clusters play the role of formed metal electrodes and can be controlled by the PCBM concentration and annealing, unlike the field-induced formed metal. *(iii) Ohmic behavior.* High PCBM concentration led to short circuiting due to formation of cluster chains or single large clusters. Finally, we have shown strong evidence that breakdown of the native aluminum oxide layer cannot solely explain the observed device behavior. The results on different device morphologies and their relation to the electrical behavior suggest, on the contrary, that PCBM/PS layer does not merely act as a passive current limiting series resistance, but it also has a strong influence on the device behavior and allows tuning of switching and NDR.

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