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This paper describes the performance of a nonvolatile memory device based on a solution-processed poly(styrene-*b*-4-vinylpyridine) (PS-*b*-P4VP) diblock copolymer thin film. The Al/PS-*b*-P4VP/indium tin oxide memory device featuring metal-coordinated 30 nm P4VP cores exhibited an ON/OFF ratio of 2×10^5, an erase voltage of 0.75 V, a write voltage of -0.5 V, and a retention time of 10^4 s. The device exhibited a metallic behavior in the ON state, suggesting the formation of metallic filaments through the migration of Al atoms into the P4VP domain during writing. Such nanostructured diblock copolymer thin films open up avenues for fabricating organic memory devices using simple procedures. © *2008 American Institute of Physics*.
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Diblock copolymers are self-assembled soft materials that can possess a variety of ordered structures—e.g., classical lamellas, hexagonal cylinders, and spheres—having periodic thicknesses ranging between 10 and 100 nm. Hence, the use of block copolymers as templates is a simple approach toward producing hierarchically ordered structures for electrical applications.[1–3] Electrically bistable nonvolatile memory devices incorporating organic materials are attracting considerable attention because of their many advantageous properties including flexibility, material variety, and low cost. Bistable organic memory devices exhibit two different conductive states that can be manipulated by controlling the voltage or current; the resulting change resistance can occur through several mechanisms, such as the trapping/detrapping of charges by nanoclusters in the insulator,[4,5] the rupture and formation of conductive filaments,[6,7] reduction/oxidation processes,[8] and intramolecular conformational changes.[9] The use of self-assembled block copolymer thin films as dielectrics or active layers in organic memory devices has been studied only rarely. In this paper, we report an electrically bistable organic device based on a self-assembled polystyrene-*b*-poly(4-vinylpyridine)(PS-*b*-P4VP) diblock copolymer thin film possessing a hexagonal nanostructure, which exhibits resistive switching characteristics relative to those of homopolymeric PS and P4VP thin films. The resistive switching behavior of the device can be modeled by considering the fact that it functions through a metallic filament mechanism.

Figure 1 displays the process we adopted to prepare a nonvolatile memory device comprising of a monolayer PS-*b*-P4VP thin film, an indium tin oxide (ITO) bottom electrode, and an Al top electrode. The PS-*b*-P4VP diblock copolymer employed (Polymer Source, Inc.) had molecular weights (M_n) of its PS and P4VP components of 46 900 and

20 600, respectively, with a polydispersity index (M_w/M_n) of 1.14. This PS-*b*-P4VP copolymer possessed a hexagonal cylinder structure in the bulk state [Fig. 1(a)] but forms a micellar structure that consists of a PS corona and a P4VP core when dissolved into 0.5 wt % in chlorobenzene [Fig. 1(b)]. This micellar PS-*b*-P4VP solution was spin coated at 3000 rpm onto an ozone-treated ITO electrode to form a monolayer PS-*b*-P4VP thin film. To obtain an ordered hexagonal P4VP assembly [Fig. 1(c)], this monolayer PS-*b*-P4VP thin film was thermally annealed at 150 °C under vacuum for 3 h. A 50-nm-thick film of Al was thermally evaporated through a shadow mask (deposition rate: 4 Å/s; pressure: 10^{-6} torr) onto the PS-*b*-P4VP film to form a top electrode. The scanning electron microscopy (SEM) image of a cross section of the Al/PS-*b*-P4VP/ITO device [Fig. 1(d)] reveals the high quality of the interfaces between the layers.
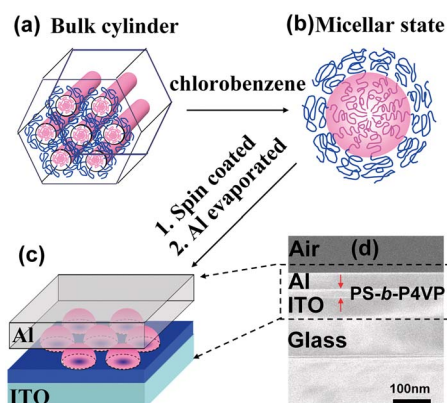
FIG. 1. (Color online) (a) Morphology of a cylindrical PS-*b*-P4VP diblock copolymer in the bulk state. (b) Micellar structure of a cylindrical PS-*b*-P4VP diblock copolymer in a selective solvent. (c) Nonvolatile memory device comprising of an active PS-*b*-P4VP diblock copolymer film and Al and ITO electrodes. (d) SEM image of the cross section of the memory device in (c).

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FIG. 2. (Color online) *I-V* characteristics of PS (◆), P4VP (■), and PS-*b*-P4VP (▲). The turn-on compliance current was restricted to 10^{-3} A. The inset displays an AFM topographic image of the PS-*b*-P4VP thin film prior to evaporating the Al electrode.

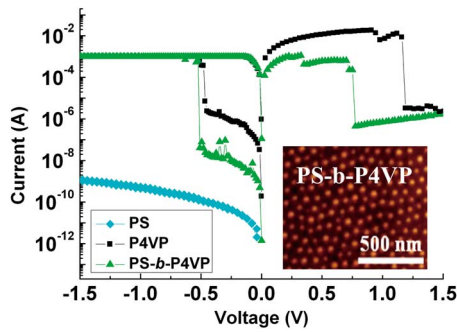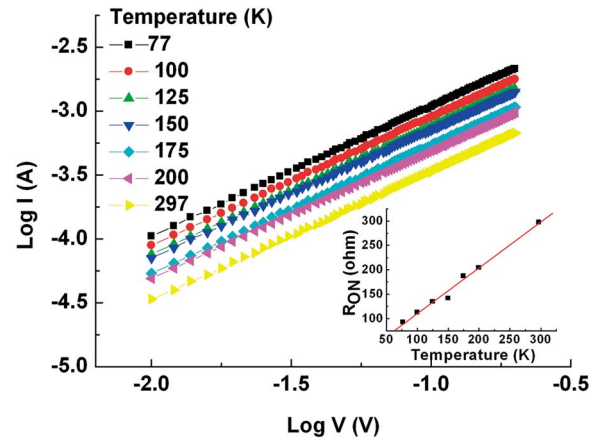FIG. 3. (Color online) Logarithmic *I-V* plots measured at various temperatures for the ON state at potentials ranging from 0.01 to 0.2 V. The inset displays the resistance of the ON state plotted with respect to the temperature.

We measured the electrical characteristic of Al/PS-*b*-P4VP/ITO, Al/PS/ITO, and Al/P4VP/ITO devices by semiconductor parameter analyzer (HP4156C, Agilent) performed on a probe station (VFTTP4, Lakeshore) under 10^{-5} torr at room temperature, and plot their semilogarithmic current-voltage (*I-V*), as displayed in Fig. 2. For the Al/PS/ITO device featuring a homogenous PS surface, the *I-V* characteristics display a low current that increased slowly upon increasing the applied voltage, indicating that PS is a good insulator that has no memory effect. In contrast, the Al/PS-*b*-P4VP/ITO, and Al/P4VP/ITO devices displayed electrical bistability with a sufficiently large sensing margin between the ON and OFF states.

The *I-V* characteristics of the Al/P4VP/ITO device initially exhibited a high-resistance state (OFF state); after performing a negative-voltage sweep to approximately −0.5 V, the device was switched to a low-resistance state (ON state). When a positive-voltage sweep was applied to approximately +1.2 V, the device switched back to its initial OFF state. The maximum ON/OFF current ratio for the P4VP device was 2×10^3 at −0.1 V. For the Al/PS-*b*-P4VP/ITO device, the turn-on and turn-off threshold voltages were −0.5 and +0.75 V, respectively; the maximum ON/OFF current ratio was 2×10^5 at −0.1 V. The atomic force microscopy (AFM) topographic image of the PS-*b*-P4VP thin film (inset in Fig. 2) reveals the microphase separation of quasihexagonal structures that resulted from the micellization of PS-*b*-P4VP; the light regions (size: approximately 30 nm) represent the P4VP domains and the dark areas represent the PS matrix.

For both the Al/PS-*b*-P4VP/ITO and Al/P4VP/ITO devices, after removing the compliance current limit, the magnitudes of the turn-off currents were larger than their turn-on compliance currents.[10] In addition, the ON state of each device could be converted into the OFF state by applying the sweeping voltage in the same direction. This behavior can be explained by considering a metallic filament theory.[11]

To prove that the metallic filamentary mechanism operates, we used a cryostat system operated under 10^{-5} torr to measure the temperature dependence of the resistance of the ON state of the Al/PS-*b*-P4VP/ITO memory devices. Figure 3 reveals that the conduction mechanism of the ON state is dominated by an Ohmic conduction ($I \propto V$). The resistance of the ON state increased linearly upon increasing the temperature—typical of metallic behavior. The equation $R = R_0[1 + \alpha(T - T_0)]$ represents the variation in the resistance with respect to the temperature, where α is the temperature

coefficient and R_0 is the resistance measured at a reference temperature T_0, usually 293 K.[12] The temperature coefficient of 0.0031 that we obtained after fitting the results in the inset of Fig. 3 is slightly smaller than the acknowledged value of 0.0043.[13] This discrepancy may be due to thermal losses occurring at the contact between the Al/PS-*b*-P4VP/ITO device and the cryoprobe.[14]

P4VP, which contains pyridyl groups, interacts strongly with Al clusters or atoms. The diffusion of these Al clusters or atoms is, however, negligible because PS has a low affinity toward this metal.[15] We suspect that Al atoms migrated into the P4VP zones to form metallic filaments and that these Al filaments grew during the writing progress. The dimensions of the P4VP nanodomains in the PS-*b*-P4VP thin film would limit the growth and size of these Al filaments, whereas a homopolymeric P4VP thin film might have no limitation to the extent of growth of similar Al filaments. In general, filaments having larger size would be more difficult to break. Thus, scaling down the size of the organic memory materials to the nanometer scale resulting from the self-assembled diblock copolymer provides the organic memory device with a higher ON/OFF ratio and lower erasing and writing voltages.

Figure 4(a) displays the time-resolved *I-V* characteristics of the Al/PS-*b*-P4VP/ITO organic memory device. The write/read/erase/read cycle was recorded using an oscilloscope (Keithley, 4200-SCP2HR) equipped with an arbitrary waveform generator (Keithley, 4205-PG2) and a programming current amplifier (Keithley, 428). In general, the switching speed depends on the amplitude of the write/erase signal. Our read/write/erase cycle sequence consisted of a 5 μs write pulse at −1.5 V, a 10 μs erase pulse at 5 V, and a 0.1 V read voltage. Applying the write and erase pulses switched the device to its ON and OFF states, respectively. Although the switching speed of this Al/PS-*b*-P4VP/ITO memory device was acceptable for its use in most consumer products, there is much room for improvement.

Our Al/PS-*b*-P4VP/ITO organic memory device was nonvolatile: it was stable and could be read many times as long as the probing voltage remained below the threshold voltage. Figure 4(b) displays the retention characteristics of our Al/PS-*b*-P4VP/ITO organic memory device, measured by monitoring the current at −0.1 V after programming and
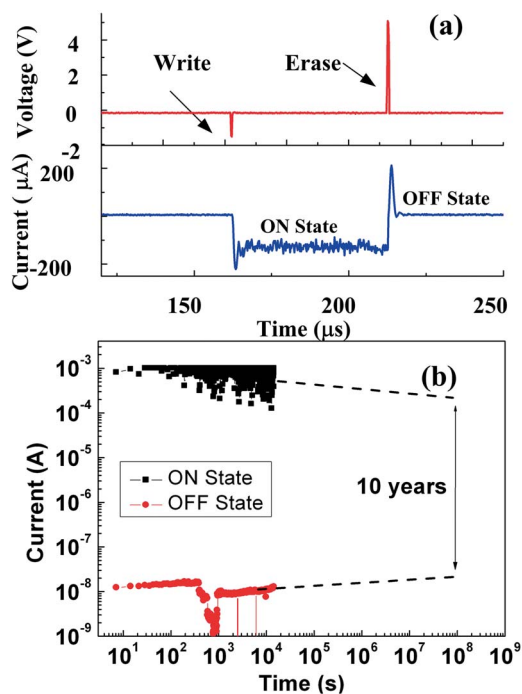
FIG. 4. (Color online) (a) Write/read/erase test of the ITO/PS-*b*-P4VP/Al organic memory device. The bottom and top curves represent the applied voltage pulse and the corresponding current response, respectively. (b) Retention times of the ON and OFF states of the ITO/PS-*b*-P4VP/Al organic memory device probed in terms of the device current after stressing.

erasing at −1.5 and 5 V, respectively, with a 100 μs pulse bias. The currents in the ON and OFF states differed by five orders of magnitude with no significant changes after 10^4 s. We extrapolated a 10 year memory window for our Al/PS-*b*-P4VP/ITO organic memory device; the memory window of approximately 10^5 is sufficient for its use in practical nonvolatile memory devices.

In summary, we have demonstrated that a device incorporating a micellar thin film of a diblock copolymer, consisting of metal-coordinated cores and insulating shells, operates through the formation of metallic filaments. This

Al/PS-*b*-P4VP/ITO organic nonvolatile memory device is switchable with a long retention time and an acceptable programming speed; notably, it exhibits a lower erase threshold voltage and a higher ON/OFF ratio than those of the corresponding Al/P4VP/ITO device. This fabrication approach opens up possibilities for improving the memory performance of polymeric materials prepared at low cost using simple processes.

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