Electrical bistabilities and memory mechanisms of organic bistable devices based on colloidal ZnO quantum dot-poly(methylmethacrylate) polymer nanocomposites

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Transmission electron microscopy images showed that colloidal ZnO quantum dots (QDs) were distributed around the surface of a polymethylmethacrylate (PMMA) polymer. Current-voltage (I-V) measurements on the Al/colloidal ZnO QDs blended with PMMA polymer layer/indium-tin-oxide/glass devices at 300 K showed a current bistability. The maximum ON/OFF ratio of the current bistability for the organic bistable devices (OBDs) was as large as $5 \times 10^4$, and the cycling endurance time of the ON/OFF switching for the OBDs was above $10^5$. The memory mechanisms of the fabricated OBDs are described on the basis of the I-V results. © 2009 American Institute of Physics. [DOI: 10.1063/1.3111445]

Nanocomposite structures containing inorganic nanoparticles have been particularly attractive because of interest in both investigations of fundamental physical properties and potential applications in next-generation electronic and optoelectronic devices operating at lower powers and higher temperatures. Hybrid inorganic/organic composites containing inorganic nanoparticles have currently emerged as excellent candidates for potential applications in next-generation nonvolatile memory devices. The prospect of promising applications of nonvolatile memory devices utilizing hybrid inorganic/organic composites containing inorganic nanoparticles has led to substantial research and development efforts to form nanoparticles acting as charging and discharging islands. Among the several types of nonvolatile memory devices, organic bistable devices (OBDs) have been particularly interesting and promising candidates for next-generation nonvolatile memory devices due to their relatively simple fabrication process without additional sources and drains. Even though some investigations concerning the memory effects in OBDs fabricated utilizing inorganic nanoparticles embedded in an organic layer fabricated by using a precisely controlled method under vacuum conditions have been performed, studies on the electrical bistabilities, the memory stabilities, and the memory mechanisms in OBDs made of synthesized ZnO quantum dots (QDs) blended with an insulating polymethylmethacrylate (PMMA) polymer fabricated by using a simple spin-coating method have not been reported yet.

Hybrid composites containing colloidal ZnO QDs and the PMMA polymer used in this study were prepared on indium-tin-oxide (ITO)-coated glass substrates by using a spin-coating technique. The ITO-deposited glass substrates were alternately cleaned ultrasonically in acetone, methanol, and ethanol at $27 ^\circ C$ for 10 min each and were rinsed in de-ionized water thoroughly. The chemically cleaned ITO-deposited glass substrates were then dried by using $N_2$ gas with a purity of 99.9999%. ZnO QDs were synthesized by modifying a simple method with the use of a dimethylformamide (DMF) reduction. The colloidal ZnO QDs used in the active regions of the device were formed. Solutions were formed by dissolving zinc acetate dehydrate $[\text{Zn(CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$ (1 wt %) in DMF in the proper proportions. After the zinc acetate dehydrate/DMF solution had been vigorously stirred for 10 min at room temperature, the mixture was heated to 105 $^\circ C$ at a heating rate of 2 $^\circ C$/min and was maintained at the same temperature for 5 h, resulting in the formation of colloidal ZnO QDs. After the synthesis of the ZnO QDs at 105 $^\circ C$ for 5 h had been finished, they were cooled to room temperature. The colloidal ZnO QDs were mixed with the PMMA solutions with concentrations of 0.5, 1.5, and 2.5 wt %. Subsequently, the ZnO QDs/PMMA solution was deposited onto an ITO film by using a spin-coating technique, which was followed by the thermal evaporation of an Al layer to a thickness of about 150 nm. A schematic diagram of the OBD fabricated in this work is shown in Fig. 1.

Figure 2(a) shows a plane-view bright-field transmission electron microscopy (TEM) image of the ZnO QDs dispersed in the DMF solution. The ZnO QDs are randomly distributed, as shown in Fig. 2(a). The inset of Fig. 2(a) presents a high-resolution TEM (HRTEM) image of the ZnO QDs. The HRTEM image shows that the sizes of the ZnO QDs are approximately 5 nm. Figure 2(b) shows a plane-view bright-field TEM image of the ZnO QDs embedded in a PMMA insulating polymer matrix with a concentration of 1.5 wt %. An apparent aggregation of the ZnQ QDs appears among the PMMA molecules, resulting in the formation of...
PMMA materials. The TEM image shows a particlelike structure of PMMA with a diameter of about 150 nm. Figure 2(b) shows an enlarged view of the ZnO QDs, indicated by arrows that were dispersed and attached on the surface of the PMMA. The HRTEM image shows that the size of the ZnO QDs embedded in the PMMA organic matrix with a size of 100 nm is approximately 5 nm.

Figure 3 shows current-voltage (I-V) curves for the Al/ZnO QDs+PMMA/ITO OBD devices with PMMA concentrations of 0.5, 1.5, and 2.5 wt %. The I-V curves for all devices clearly show clockwise electrical hysteresis behaviors, which are essential features for bistable devices. State “1” and state “0” correspond to the relatively high-current (ON state) and the relatively low-current states (OFF state), respectively. The bistable transition from the “OFF” state to the “ON” state is equivalent to the “writing” process in a digital memory cell. After the transition is achieved, the ON state remains in the device even after the power is turned off, which is shown in the reverse bias voltage denoted by the upper empty circles shown in Fig. 3. The OFF state can be achieved by applying a reverse bias voltage. This is equivalent to the “erasing” process of a digital memory cell. The maximum current ratio between the ON and the OFF states for the Al/ZnO QDs+PMMA/ITO device with a PMMA concentration of 1.5 wt % at 1 V is as large as about 5 × 10^4, which is equivalent to a reading process in a digital memory cell. The ON/OFF current ratio for the device with a PMMA concentration of 1.5 wt % is much larger than that for the devices with a PMMA concentration of 0.5 wt %. Therefore, the storage capability of the device is significantly enhanced with increasing concentration of the PMMA molecules. However, the maximum ON/OFF current ratio for the device with a PMMA concentration of 2.5 wt % is much smaller than that for the device with a PMMA concentration of 1.5 wt % due to the formation of large aggregations of ZnO QDs among the PMMA molecules. The optimized OBD device with a PMMA concentration of 1.5 wt % transits from the OFF state to the ON state at an applied voltage of 1.25 V. When the device current is decreased by four orders of magnitude, the state of the device returns to its initial OFF state by sweeping from +1.25 to −1.25 V. The threshold voltage of the OBDs at the transition state is about −1.25 V, which can be defined as the “erasing voltage” for the device.

Write-read-erase-read measurements were performed in air in order to investigate the rewritable nonvolatile memories of the OBDs. The write, read, and erase voltages for the I-V characteristics in Fig. 3 were set as 2, 1, and −2 V, respectively, as shown in Fig. 4(a). An applied voltage pulse of 2 V drives the device to the ON state with a current level of 10^-9 A. The current at a read voltage of 1 V is approximately 10^-10 A. After the positive write and read pulses, a voltage pulse of −2 V is applied to erase the memory device to the ON state. This OFF state is detected by using a detect pulse of 1 V with a current around 10^-6 A. The difference between the current levels shown in Figs. 3 and 4(a) is primarily attributed to the operation difference between the pulse and the direct current modes. A sequence of pulses in less than 0.001 s was used to confirm memory stability. The currents as functions of the number of cycles for the ON and the OFF states of the OBDs are demonstrated in Fig. 4(b). A cycling endurance of over 10^5 times of ON/OFF switching, together with a rewriting capability, is important for practical applications in memory devices. The memory retention ability was tested by leaving the OBDs in the ON state under ambient conditions. The ON state of the OBDs was maintained during 10^5 cycles. The stability of the OBDs under stress was evaluated for a continuous applied bias. After a constant voltage of 1 V had been applied to the OBDs in the OFF state and the ON state, the current was recorded at different times. No significant degradation of the devices in either the OFF or the ON state after 10^5 cycles of continuous stress was observed, as shown in Fig. 3, which is indicative of the memory stability of the OBDs. The endurance cycle of
ergy gap acts as a carrier blocking material, resulting in the molecules along the direction of the applied bias voltage through the LUMO level are transported among the PMMA molecules. Fowler–Nordheim tunneling process, the electrons existing at the valence band of the ZnO QDs from the Al into the LUMO level occurs through the field are released into the PMMA matrix and then transported to the Al electrode through the Fowler–Nordheim tunneling process, the erasing process is performed. The generated internal electric field disappears due to the emission of the electrons captured in the ground-state electronic subband of the ZnO QDs into the Al electrode. This is equivalent to the erasing process of a digital memory cell.

In summary, OBDs based on hybrid QD-polymer memory devices were demonstrated. The I–V curves at 300 K for the Al/hybrid ZnO QDs-PMMA/ITO devices exhibited electrical bistable behaviors. TEM images showed that ZnO QDs were formed on the surface of the PMMA molecules and in the PMMA polymer. The maximum ON/OFF current ratio of the electrical bistability for the OBDs was as large as $5 \times 10^5$, and the cycling endurance time of the ON/OFF switching for the OBDs was above $10^5$.

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The OBDs is comparable with that of the commercial flash memory devices. Even though the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) levels for the PMMA layer are not reported, the energy gap is estimated to be 5.6 eV from the optical absorption of the material. The PMMA polymer with a large energy gap acts as a carrier blocking material, resulting in the blockage of holes due to the relatively large energy barrier between the work function of the ITO electrode and the HOMO level of the PMMA layer. When a positive applied voltage is applied to the electrode, after the injection of electrons from the Al into the LUMO level occurs through the Fowler–Nordheim tunneling process, the electrons existing at the LUMO level are transported among the PMMA molecules along the direction of the applied bias voltage through the tunneling process. This results in the achievement of the writing process. The electrons actually encounter ZnO QDs with increasing electric field to a certain value, and they traverse the hybrid composites, resulting in a tunneling of the holes through the valence band of the ZnO QDs. Therefore, the ZnO QDs and the PMMA layer are charged positively and negatively, respectively, resulting in the formation of an internal electric field along the same direction as that of the applied voltage. On the contrary, when a negative voltage is applied to the electrode, because the electrons captured in the valence band of the ZnO QDs under the negative electric field are released into the PMMA matrix and then transported to the Al electrode through the Fowler–Nordheim tunneling process, the erasing process is performed.

FIG. 4. (a) Write-read-erase-read sequence operation of the Al/hybrid ZnO QDs-PMMA/ITO devices; the sequence of the voltage pulse is 2, 1, –2, and 1 V. (b) Currents as functions of the number of cycles for the ON and the OFF states of the OBDs.

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