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Electrical bistabilities and operating mechanisms of memory devices fabricated utilizing ZnO quantum dot–multi-walled carbon nanotube nanocomposites

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Abstract
Transmission electron microscopy images showed that the ZnO quantum dots (QDs) were conjugated with multi-walled carbon nanotubes (MWCNTs). Bistable memories utilizing an ensemble of the ZnO QD–MWCNT heterostructures were developed and the storage capability of the devices was significantly enhanced due to the conjugation of the ZnO QDs and the MWCNTs. Operating mechanisms of memory devices fabricated utilizing the ZnO QD–MWCNT heterostructures are described on the basis of the current–voltage results. The memory devices exhibited excellent environmental stability at ambient conditions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nonvolatile nanoscale memory devices have been the focus of significant research interest owing to their potential application in next-generation memories with higher information density and operating stability [1–5]. The quantum confinement of charge carriers in nanoscale materials, combined with their deliberate engineering of the energy-band alignment, underlie the excellent performance in nanoscale memories, which is superior to that of traditional silicon-based microelectronics [6]. Thus, the efficiency enhancement of carrier injection and trapping in the nanocomposites plays a very important role in enlarging the storage capacity of nonvolatile memory devices. To date, various kinds of nonvolatile memory devices utilizing nanoscale materials have been proposed to investigate the feasibility of nanoelectronic devices [7–11]. However, the connection between improvement of charge injection and trapping, and devices fabricated utilizing hybrid nanocomposites still faces substantial challenges.

Carbon nanotubes (CNTs) have drawn a great deal of interest because of their remarkable structure-dependent electronic properties [12]. The electrical properties of multi-walled CNTs (MWCNTs) exhibit either metallic or semiconducting properties, depending on their folding angle, diameter and outermost shell [13–16]. CNTs with great mechanical toughness and chemical inertness have emerged as promising materials for creating reliable, fast-response memory devices operating at lower currents and higher temperatures.

The main concept for integrated nanoscale memories in this work differs substantially from previous efforts because it exploits an ensemble of QD/CNT heterostructures for switchable and bistable device elements with well-defined low-current 'OFF' and high-current 'ON' states. Firstly, acid-treated MWCNTs were used to form a uniform and amorphous film, acting as the host for nanoscale QDs. The introduction of MWCNTs provides an effective pathway for carrier transport and capture, and the chemical inertness of the MWCNTs enables the high operating stability of the fabricated memories. Secondly, the QDs, acting as carrier trap regions, are attached to the surfaces of MWCNTs through covalent

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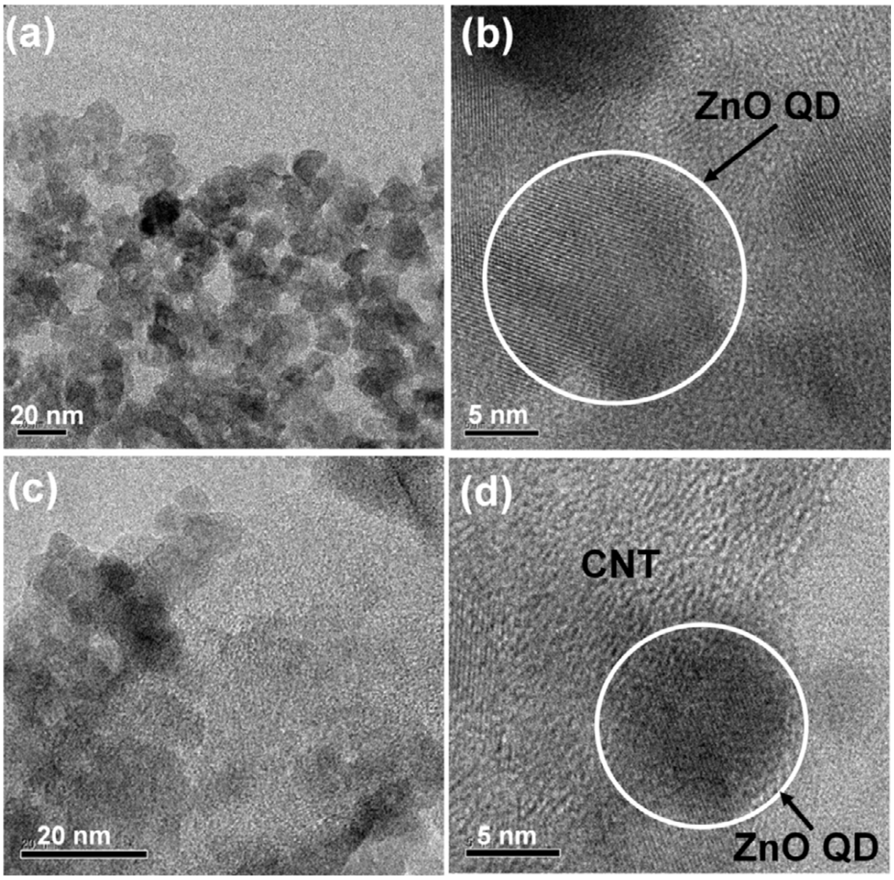

Figure 1. High-resolution transmission electron microscopy images of (a) ZnO QDs synthesized from an aqueous solution, (b) a single ZnO QD with a size of 6 nm, (c) an individual MWCNT after the assembled ZnO quantum dots and (d) a single ZnO quantum dot attached on the surface of the MWCNT.

chemical bonds. The conjugation of the QD to the MWCNT creates an effective carrier transfer channel, resulting in an improved carrier capture efficiency. A device element can be switched between these well-defined ON and OFF states, and the variation in the carrier transfer efficiency can be seen by observing the ratio of the ON to the OFF currents.

This paper reports data for the electrical bistabilities and the operating mechanisms of nonvolatile memory devices fabricated utilizing self-assembled ZnO QDs on the surfaces of acid-treated MWCNTs. High-resolution transmission electron microscopy (HRTEM) measurements were carried out to investigate the existence and the microstructural properties of hybrid ZnO QD and MWCNT nanocomposites. Current–voltage (I–V) measurements on the devices based on hybrid ZnO QD and MWCNT nanocomposites were performed to investigate their carrier transfer and the bistable behavior of the memory devices.

2. Experimental details

MWCNTs (purchased from Aldrich) were oxidized in nitric acid at 60 °C for 30 h. The acid-treated MWCNTs were rinsed thoroughly in distilled water and were finally collected by using a filter. The filtered MWCNT cake was dried by heating at 100 °C for 24 h. The acid treatment, apart from introducing acid groups at the side walls of the CNTs, oxidized the graphitic impurities present along with the MWCNTs [17]. 10 ml of dimethyl formamide (DMF) was used as a solvent, in which 10 mg of acid-treated MWCNTs were uniformly dispersed by ultrasonication. Zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$], 0.23 g, was dissolved in 50 ml of DMF, then the MWCNT solution was added with continual stirring to form a stable precursor. Subsequently, the mixed solution was heated to 95 °C by using the water bath in order to achieve a low heating rate and was maintained at that temperature for 5 h. After the heating process, the mixture was kept in a water bath until it had cooled. Finally, the hybrid ZnO QD and MWCNT nanocomposites were obtained by using a filter; simultaneously, ZnO QDs could be harvested as a solution in DMF with excellent transparency. A stable suspension of the hybrid ZnO QD and MWCNT nanocomposites could be obtained by using chloroform as solvent. The indium-tin-oxide (ITO)-coated glass, acting as a substrate and as an electrode in the memory devices, was alternately cleaned with a chemical cleaning procedure by using trichloroethylene, acetone, and methanol. An Al layer with a thickness of 300 nm was formed by using thermal evaporation after the active layer consisting of hybrid ZnO QD and MWCNT nanocomposites had been formed by using a spin-coating technique. A sample without ZnO QDs (Al/MWCNTs/ITO) and a sample using the mixture of MWCNTs and collected ZnO QDs (Al/ZnO QDs–MWCNTs mixture/ITO) were fabricated as references to which the

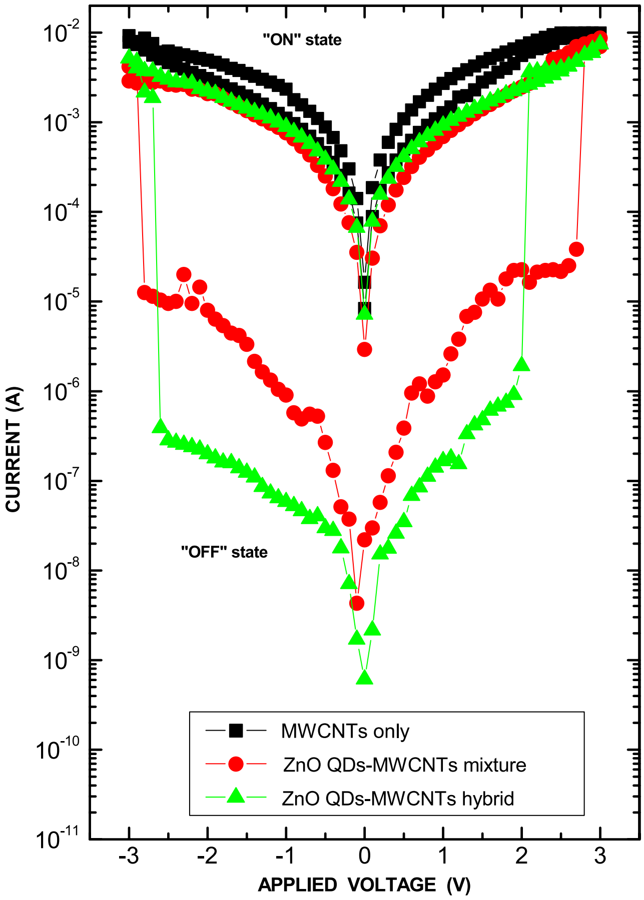

Figure 2. Current–voltage characteristics of the Al/MWCNTs/ITO, the Al/ZnO QD–MWCNT mixture/ITO and Al/ZnO QD–MWCNT hybrid nanocomposite/ITO devices.

electrical properties of the devices containing hybrid ZnO QD and MWCNT nanocomposites could be compared.

3. Results and discussion

An HRTEM image of as-grown ZnO QDs with a mean particle size of 5–6 nm is shown in figure 1(a) and an HRTEM image of a single ZnO QD is shown in figure 1(b). Figure 1(c) shows an HRTEM image of an individual QD/MWCNT heterostructure, in which side-wall conjugations are clearly observed, and figure 1(d) shows that ZnO QDs are randomly attached on the surfaces of the MWCNTs [18]. The crystalline ZnO QDs might be formed on defect-like sites of the acid-treated MWCNTs. Even though it is not clear whether the defects of the MWCNTs are intrinsic or are introduced during the acid treatment, the defects of the MWCNTs appear to induce preferentially the nucleation of the ZnO QDs [19].

The electrical characterization of the nonvolatile memory devices based on the hybrid ZnO QD and MWCNT nanocomposites plays an important role in improving the device performance. Figure 2 shows the I–V characteristics measured from -3 to 0 V, 0 to 3 V, 3 to 0 V, and 0 to -3 V for the Al/MWCNTs/ITO, the Al/ZnO QD–MWCNT mixture/ITO and the Al/hybrid ZnO QD and MWCNT nanocomposite/ITO devices. The ON and OFF states correspond to the relatively high-current and the relatively low-current states, respectively. The I–V curves for the devices containing ZnO QDs (filled circles for the ZnO QD–MWCNT mixture and filled triangles for the hybrid ZnO QD and MWCNT nanocomposites) show an electrical hysteresis behavior, which is an essential feature for a bistable device [20]. The I–V measurements were performed on the device without ZnO QDs under the same conditions to investigate the charge-storage role of the ZnO QDs. The current difference between the ON and OFF states for the MWCNT-only device is negligible in comparison with that for the devices containing ZnO QDs, indicating that the electrical bistability of the hybrid ZnO QD and MWCNT nanocomposite devices can be attributed to charge transfer and capture in the ZnO QDs. The I_{ON}/I_{OFF} ratio for the Al/hybrid ZnO QD and MWCNT nanocomposite/ITO device is approximately 10^4, which is about two orders larger than that for the structure without conjugation of ZnO QDs. Furthermore, the threshold voltage of the bistable transition from the low-conductivity OFF state to the high-conductivity ON state decreases from 2.5 to 2.0 V after conjugation of the ZnO QDs and the MWCNTs. These results indicate that the carrier-storage capability in the hybrid bistable devices is significantly improved due to the enhanced carrier transfer efficiency between the QDs and the MWCNTs.

A dendritic carrier transfer model for the operating mechanism of the nonvolatile bistable devices based on hybrid ZnO QD and MWCNT nanocomposites can be described on the basis of the I–V results. The electrons injected from the Al electrode move on the outermost shell along the CNT under an applied electric field [21]. The transported electrons actually encounter dangling ZnO QDs and transfer to the conduction bands of the ZnO QDs through the covalent bond between the MWCNT and the ZnO QDs with increasing electrical field up to a certain value. The conjugation of ZnO QDs on the surfaces of the MWCNTs provides a carrier transfer channel that significantly enhances the electron transfer efficiency of the Al/hybrid ZnO QD and MWCNT nanocomposite/ITO devices, resulting in a significant increment in the I_{ON}/I_{OFF} ratio. The attachment of a large number of ZnO QDs on the surfaces of the MWCNTs enables the realization of the dendritic carrier transfer and capture process, as shown in figure 3. The trapped electrons generate an internal electric field along the direction of the applied voltage [22], resulting in the appearance of the high-conductivity ON state shown in figure 2. When a negative voltage is applied to the device, the electrons captured in the CdSe/ZnS QDs are released to the MWCNT backbone and then transported to the gate electrode, resulting in the performance of the erasing process.

The memory retention ability of the device fabricated utilizing hybrid ZnO QD and MWCNT nanocomposites is very important in achieving high-performance devices for practical applications. Figure 4 shows the current as a function of time for the Al/hybrid ZnO QD and MWCNT nanocomposite/ITO device in the ON state under a constant bias of 0.5 V. Ageing tests were performed by keeping our device in the high-current-conducting ON state under ambient conditions. The device remained in the ON state for several days to weeks

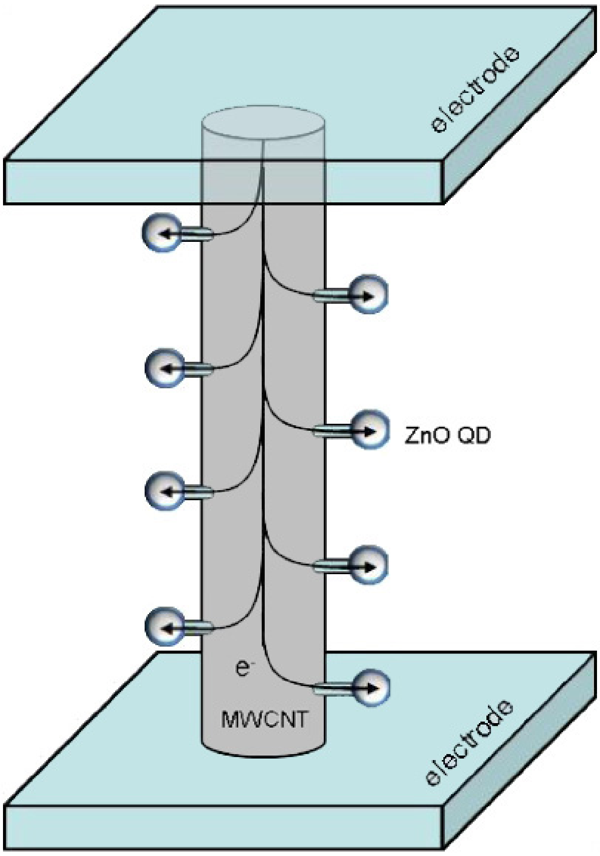

Figure 3. Schematic diagram of the dendritic carrier transfer and trapping between the MWCNTs and the ZnO QDs under an electric field.

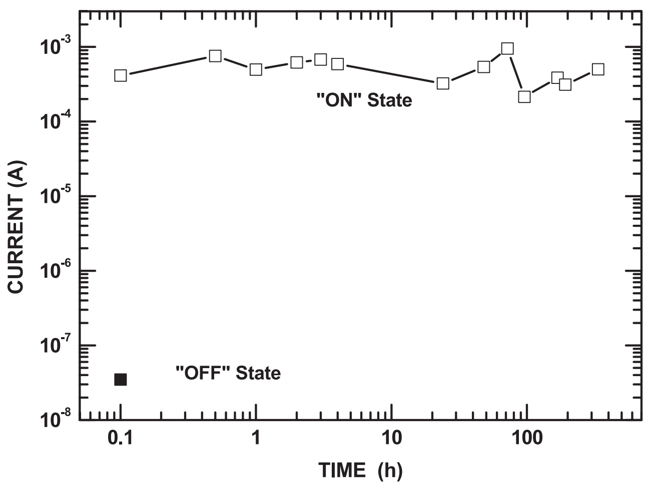

Figure 4. Current as a function of time for the Al/ZnO QD–MWCNT hybrid nanocomposite/ITO device in the ON state under a constant bias of 0.5 V.

without any significant degradation, as shown in figure 4. This result indicates that the device fabricated in this work exhibits excellent environmental stability under ambient conditions.

4. Summary and conclusion

The self-assembled ZnO QDs conjugated on the surfaces of acid-treated MWCNTs were realized under mild reaction conditions. HRTEM images clearly showed side-wall conjugation of the ZnO QDs and the MWCNTs. The I–V curves at ambient temperature for the Al/hybrid ZnO QD and MWCNT nanocomposite/ITO devices exhibited a nonvolatile electrical bistable behavior. The enhancement in the memory-storage capacity for the nonvolatile memory devices fabricated utilizing hybrid ZnO QD and MWCNT nanocomposites should be due to the creation of a carrier transfer channel between the ZnO QDs and the MWCNTs. A dendritic carrier transfer model for the nonvolatile bistable devices based on the hybrid ZnO QD and MWCNT nanocomposite was described on the basis of the I–V results. Memory retention under ambient conditions exhibited good stability. The results indicated that the reversible and bistable devices fabricated utilizing the hybrid ZnO QD and MWCNT nanocomposites hold promise for potential applications in next-generation nonvolatile memories.

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