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Memory mechanisms of nonvolatile organic bistable devices based on colloidal $CuInS_2$/ZnS core–shell quantum dot – Poly(N-vinylcarbazole) nanocomposites

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ABSTRACT

Organic bistable devices (OBDs) fabricated utilizing $CuInS_2$ (CIS)/ZnS core–shell-type quantum dots (QDs) blended with a poly(N-vinylcarbazole) (PVK) layer were fabricated on polyethylene terephthalate (PET) substrates by using a spin-coating technique. Transmission electron microscopy images revealed that the CIS/ZnS QDs were distributed over the surface of the PVK layer. Current–voltage (*I–V*) curves for the Al/PVK + [CIS/ZnS QDs]/ITO/PET devices at 300 K showed that the maximum ON/OFF ratio of the current bistability for the OBDs was as large as 3.9×10^4. Memory mechanisms for the OBDs fabricated on PET substrates are described on the basis of the *I–V* results.

The formation and the physical properties of hybrid inorganic/organic nanocomposites containing inorganic nanoparticles have been studied extensively because of interest in investigations of fundamental physics [1,2] and because of their potential applications in next-generation electronic and optoelectronic devices operating at lower powers and higher temperatures [3–6]. The prospect of promising applications of nonvolatile memory devices utilizing hybrid inorganic/organic nanocomposites containing inorganic nanoparticles has led to substantial research and development efforts to form inorganic nanoparticles, acting as charging and discharging islands, embedded in a polymer layer [7–14]. Among the several types of core–shell inorganic nanoparticles, $CuInS_2$ (CIS)/ZnS core–shell quantum dots (QDs) have emerged as excellent candidates due to their promising applications in next-generation nonvolatile memory devices and to their being environment-friendly materials in comparison with core–shell QDs containing Cd and Pb atoms, such as CdSe/ZnS, CdSe/PbS, and CdSe/Ag_2S core–shell QDs. While the Restriction of Hazardous Substances Directive (RoHS) prohibits the utilization of compound semiconductor materials containing Cd and Pb atoms in devices, the RoHS permits the use of CIS/ZnS materials [15]. Organic bistable devices (OBDs) have become particularly interesting because of their potential applications and their relatively simple fabrication process without additional sources and drains [16–18]. Even though some studies concerning the electrical properties of OBDs fabricated utilizing hybrid inorganic/organic nanocomposites containing metal or semiconductor nanoparticles formed on solid-state substrates have been performed [19,20], studies on the electrical properties and the memory mechanisms of OBDs fabricated utilizing synthesized colloidal CIS/ZnS core–shell QDs blended with a poly(N-vinylcarbazole) (PVK) layer on flexible substrates by using a simple spin-coating method have not been reported yet. Furthermore, nanocomposites based on a PVK organic layer containing core–shell CIS/ZnS QDs

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formed on flexible substrates have been particularly attractive due to their potential applications in environment-friendly nonvolatile memory devices with low-power consumption and with flexible storage elements.

This letter reports data on the electrical bistability properties and the memory mechanisms of OBDs fabricated utilizing CIS/ZnS core–shell QDs blended with a PVK layer on indium-thin-oxide (ITO)-coated polyethylene terephthalate (PET) substrates by using a spin-coating method. Transmission electron microscopy (TEM) measurements were performed to investigate the structural properties of the colloidal CIS/ZnS core–shell QDs blended with a PVK layer. Current–voltage (I–V) measurements and data fitting were carried out to investigate the electrical bistability and the memory mechanisms of the Al/PVK + [CIS/ZnS QDs]/ITO/PET devices, and the memory mechanisms of the OBDs fabricated on flexible PET substrates are described on the basis of the I–V results.

The inorganic/organic nanocomposites consisting of colloidal CIS/ZnS QDs and a PVK conducting polymer layer used in this study were prepared on ITO-coated PET substrates by using a spin-coating technique. The PVK polymer was purchased from the Sigma–Aldrich Co., and the molar mass of the PVK was approximately 25,000 g/mol. The substrates were ultrasonically cleaned by using acetone and methanol and were thoroughly rinsed in deionized water. The chemically-cleaned substrates were then dried by using N_2 gas with a purity of 99.9999% in order to avoid interaction with air. The formation process of the CIS/ZnS QDs solution was started by using a CIS core solution. That solution consisting of 8 ml of octadecene (ODE), 0.1 mmol of indium acetate, and 0.3 mmol of miristic acid was mixed in a 25-ml three-neck flask. Then, the mixed solution was degassed at 110 °C for 2 h, and a Cu-thiol stock solution at 250 °C was added. Subsequently, the solution was heated at 200–210 °C for 2 h. Copper iodide, 0.3 mmol, was mixed with dodecanethiol, 3 ml, for the synthesis of the Cu-thiol stock solution. Then, the mixed solution, while being stirred, was slightly heated on a hot plate. When the synthesis of the CIS core solution was finished, the synthesized solution was in situ cooled to form the ZnS shell at room temperature. Zn acetate, 0.5 mmol, was added to the CIS core solution, and the solution was heated to 230 °C. Then, the solution was aged for 1.5 h at 230 °C.

To fabricate the CIS/ZnS core–shell QDs blended with a PVK layer, we added 2 mg of a $CuInS_2$/ZnS QDs solution to 50 mg of PVK dissolved in 5 ml of toluene. Then, the mixed solution was ultrasonicated for 30 min to obtain a uniform solution. After the substrate had been mounted onto a susceptor in the spin coater, the mixed solution was coated on the substrate by using a spin-coating method at 2500 rpm for 25 s. Then, the solvents existing on the samples were removed by putting the samples onto a hot plate at 90 °C for 30 min. Finally, Al top electrodes with thicknesses of 180 nm were thermally deposited through a metal mask at a system pressure of 1×10^{-6} torr. The diameter of the top Al electrode was approximately 0.3 mm, and the area of the bottom electrode was 2 cm × 2 cm. A schematic diagram of the OBDs fabricated utilizing CIS/ZnS QDs blended with a PVK layer is shown in Fig. 1(a).

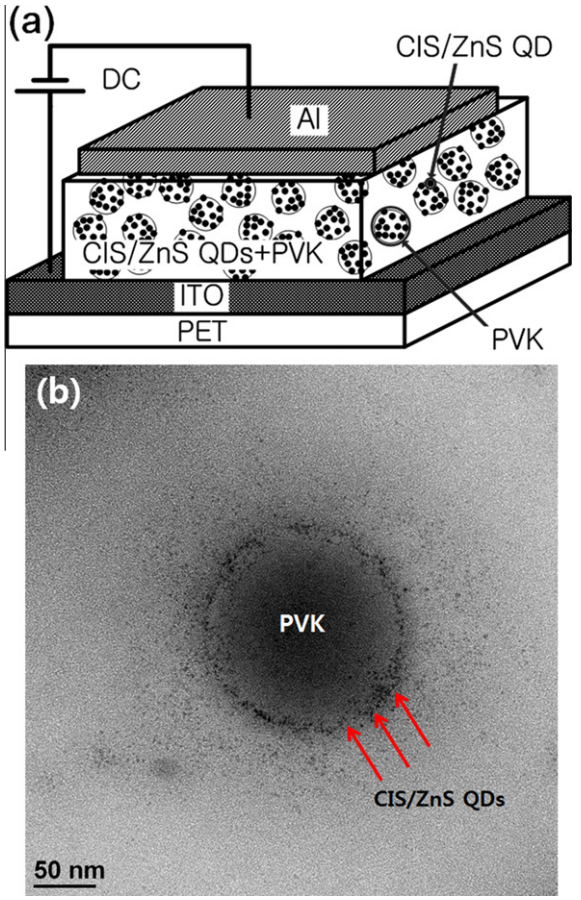

Fig. 1. (a) Schematic diagram of the OBDs based on CIS/ZnS core–shell QDs blended with a PVK polymer. (b) Plane-view bright-field transmission electron microscopy image of CIS/ZnS core–shell QDs blended with a PVK polymer.

TEM measurements (model: STEM/TEM (CM30)) were done at 200 kV. The samples for the TEM measurements were prepared by cutting and polishing with diamond paper to a thickness of approximately 30 μm and then argon-ion milling at liquid-nitrogen temperature to electron transparency. I–V measurements were performed by using a HP 4140B I–V meter at room temperature in an atmosphere.

Fig. 1(b) shows a plane-view bright-field TEM image of the CIS/ZnS QDs blended with a PVK polymer matrix. An apparent aggregation of the CIS/ZnS QDs appears around the surfaces of the PVK molecules. The TEM image indicates that the PVK has particle-like features with diameters of about 150 nm. Fig. 1(b) shows that the CIS/ZnS QDs, indicated by arrows, were attached to the surface of a PVK particle-like structure. The average diameter of the CIS/ZnS QDs is approximately 3 nm.

Fig. 2 shows the I–V curves for the Al/PVK + [CIS/ZnS QDs]/ITO/PET device. The voltage across the device was varied from −3.5 to 3.5 to −3.5 V in all cases, as shown in Fig. 2. When the bottom ITO layer is biased positive, the bias condition is forward. The I–V curves for the device clearly show current hysteresis behaviors, which are