

HYBRID INORGANIC/ORGANIC NANOCOMPOSITES CONSISTING OF CUINS₂-ZNS CORE-SHELL QUANTUM DOTS EMBEDDED IN A POLY(METHYLMETHACRYLATE) MATRIX

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Abstract

CuInS₂ (CIS) - ZnS core-shell quantum dots (QDs) were formed by a using sol-gel method, and nanocomposites consisting of CIS-ZnS core-shell QDs embedded in the poly(methymethacrylate) (PMMA) matrix were formed by a using spin-coating method. A absorption peak at 550 nm for the absorbance spectra corresponded to the optical excitation edge of the CIS-ZnS core-shell QDs. A peak at 700 nm for the PL spectrum was related to the recombination luminescence of the CIS-ZnS core-shell QDs. Capacitance-voltage curves for Al/CIS-ZnS QDs embedded in PMMA/p-Si device showed a hysteresis behavior with a flat band voltage shift.

1. Introduction

Hybrid inorganic/organic nanocomposites have been currently receiving considerable attention because of their promising applications in flexible electronic devices operating at lower powers [1-7]. The prospect of potential applications in electronic devices has led to substantial research and development efforts to form various nanocomposites containing inorganic nanocomposites, acting as charge storage regions [8-12]. Nanocomposites containing core-shell quantum dots (QDs) have emerged as excellent candidates for promising applications in electronic devices. Among the several types of QDs, CuInS₂(CIS)-ZnS ternary core-shell QDs have been particularly interesting

due to their being environment-friendly materials in comparison with core-shell QDs containing Cd and Pb atoms and to their promising applications in next-generation electronic devices. Even though some studies concerning the formation and the materials characteristics of binary core-binary shell QDs/polymer nanocomposites have been conducted [13-16], very few works on the formation and the applications of the ternary core-binary shell QDs/polymer nanocomposites have been performed. This paper reports data for formation processes and feasibility results of the hybrid nanocomposites consisting of CIS-ZnS core-shell QDs embedded in the poly(methymethacrylate) (PMMA) matrix for possible applications in nonvolatile memory devices. Absorbance and photoluminescence (PL) measurements were carried out to investigate the optical properties of CIS-ZnS core-shell QDs. Capacitance-voltage (C-V) measurements were performed to investigate the possibility for applications of nanocomposites consisting of core-shell CIS-ZnS QDs embedded in a PMMA matrix in nonvolatile memory devices.

2. Experimental Details

Inorganic/organic nanocomposites consisting of the colloidal CIS-ZnS QDs and the PMMA polymer layer used in this study were prepared on p-Si (100) substrates. The formation process of the CIS-ZnS QDs solution was started by using a CIS core solution [17]. The solution consisting of 8 ml of

octadecene (ODE), 0.1 mMol of indium acetate, and 0.3 mMol of miristic acid were mixed in a 25-ml three-neck flask. Then, the mixed solution was degassed at 110°C for 2 h and was injected with a Cu-thiol stock solution at 250°C. The schematic diagrams of the formation processes of the CIS-ZnS core-shell QDs are shown in Fig. 1. Subsequently, the solution was heated at 200-210°C for 2 h. 0.3 mMol of copper iodide, was mixed with 3 ml of dodecanethiol, for the synthesis of the Cu-thiol stock solution. Then, the mixed solution was slightly heated on a hot-plate while being stirred. After 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 PMMA layer, The 150 mg PMMA polymer insulator was dissolved in chlorobenzene (4.85 g) solvent for a 3 wt% PMMA solution. Then, CIS-ZnS core-shell QDs (5.5 mg) blended into PMMA solution. Subsequently, ultrasonication was performed for over 1 h to obtain uniform solutions. The blended solutions treated by using ultrasonic were spin-coated on p-Si substrates. The schematic diagrams of the formation processes of the nanocomposites of the CIS-ZnS core-shell QDs embedded in a PMMA are shown in Fig. 2.

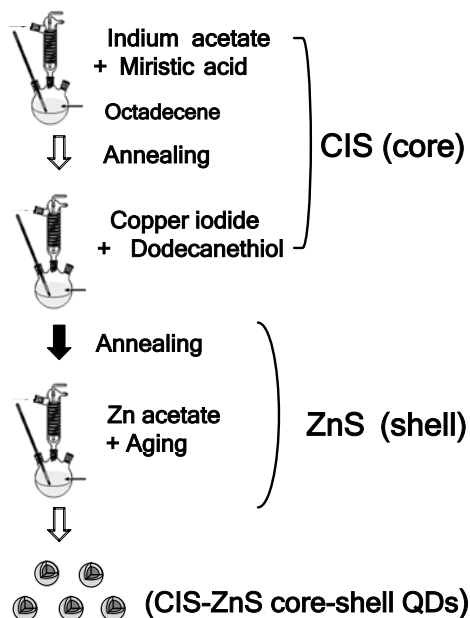


Fig. 1. A schematic of the formation processes of the CIS-ZnS core-shell QDs.

The schematic diagrams of (a) the CIS-ZnS core-shell nanoparticles and (b) nanocomposites of CIS-ZnS core-shell QDs embedded in PMMA matrix and the chemical structure of the PMMA layer are shown in Fig. 3 [18].

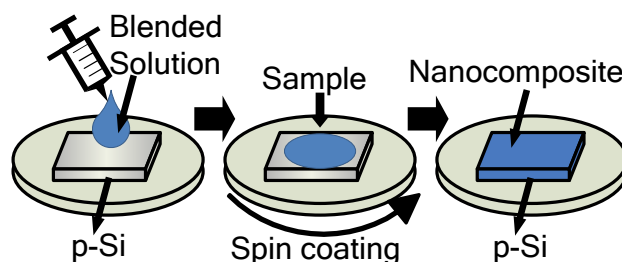


Fig. 2. A schematic of the formation processes of nanocomposites consisting of the CIS-ZnS core-shell QDs.

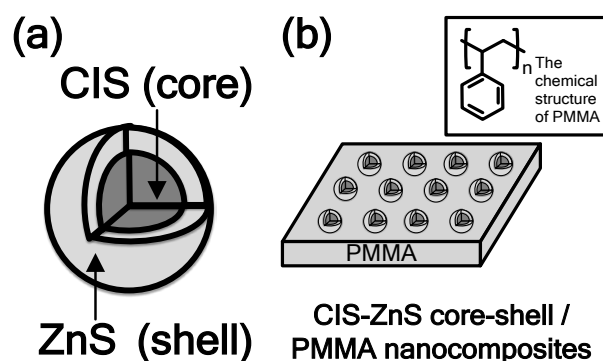


Fig. 3. (a) Schematic diagrams of the CIS-ZnS QDs and (b) nanocomposites consisting of CIS-ZnS QDs embedded in a PMMA matrix and the chemical structure of PMMA.

The optical absorption measurements were performed by using an ultraviolet-visible spectrometer (Scinco PDA S-3100). The PL measurements were carried out using a 75 cm monochromator equipped with a GaAs photomultiplier tube (Ocean Optics usb-400). The excitation source was the 355 nm line of a CWUV laser. C-V measurements were performed by using an HP 4284 precision LCR meter at room temperature.

3 Results and Discussion

Figure 4 shows optical absorbance and PL spectra of CIS-ZnS core-shell QDs. The broad absorption peak

at 550 nm for the absorbance spectrum corresponds to the optical excitation edge of the CIS-ZnS core-shell QDs [17, 19]. The dominant peak at 700 nm for the PL spectrum is related to the recombination luminescence due to the interband transitions of the CIS-ZnS core-shell QDs [17, 19]. The Stöck shift corresponding to the difference of the peak position between the absorbance and the PL spectra might be attributed to the quantum confinement effect of the CIS-ZnS core-shell QDs, but that is not yet clear.

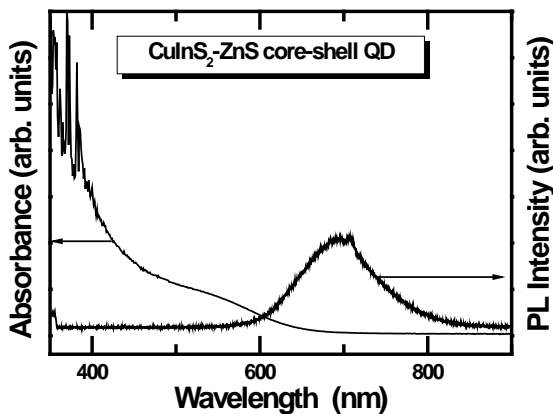


Fig. 4. Optical absorbance and photoluminescence spectra of CIS-ZnS core-shell QDs.

Al top and bottom electrodes with a thickness of 180 nm were thermally deposited in order to investigate the memory effects of the devices through a metal mask at a system pressure of 1×10^{-6} Torr. Figure 5 shows the C-V curves measured at 1-MHz for the Al/core-shell CIS-ZnS QDs embedded in PMMA layer/p-Si device at room temperature. The C-V behavior of the devices based on the CIS-ZnS QDs embedded in a PMMA layer is similar to those of metal-insulator-semiconductor diodes with floating gates containing nanoparticles [20]. The C-V curves for the Al/core-shell CIS-ZnS QDs embedded in PMMA layer/p-Si device, obtained by sweeping the applied voltage between the inversion and the accumulation regions at room temperature, clearly show counterclockwise hysteresis behavior. The appearance of the C-V hysteresis indicates the existence of charge sites occupied by electrons injected from the inversion layer in the p-Si substrate. However, the Al/PMMA/p-Si device without the core-shell CIS-ZnS QDs shows no hysteresis under same measurement conditions, indicative of the charge storage in the core-shell

CIS-ZnS QDs embedded in a PMMA layer. The memory effect of the counterclockwise hysteresis is attributed to electrons tunneled from the p-Si substrate through PMMA matrix layer and trapped in the core-shell CuInS₂-ZnS QDs [21].

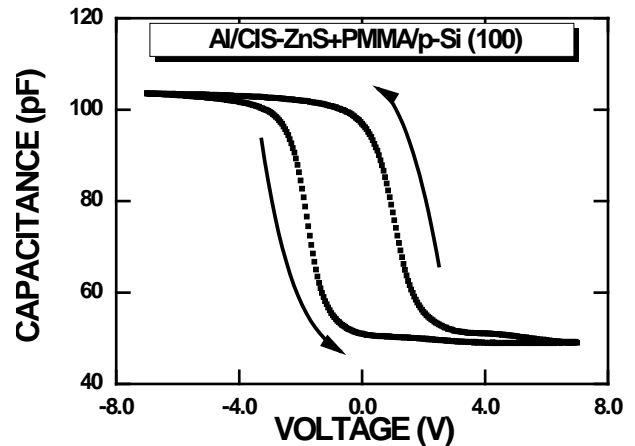


Fig. 5. C-V curves at 9 V with 1-MHz for the CIS-ZnS QDs blended in PMMA/p-Si device.

4. Summary and Conclusions

CIS-ZnS core-shell QDs were formed by using a sol-gel method, and the hybrid nanocomposites consisting of CIS-ZnS core-shell QDs embedded in the PMMA matrix were formed on p-Si (100) substrates by using a spin-coating method. The broad absorption at 550 nm for the absorbance spectrum corresponded to the optical excitation edge of the CIS-ZnS core-shell QDs. The dominant peak at 700 nm for the PL spectrum was related to the recombination luminescence due to the interband transitions of the CIS-ZnS core-shell QDs. C-V characteristics of the devices fabricated utilizing CIS-ZnS core-shell QDs embedded in a PMMA matrix showed that the hysteresis behavior of the C-V curves was attributed to the carriers captured in the CIS-ZnS QDs. The nanocomposites based on the CIS-ZnS QDs in the PMMA matrix offer possible applications in nonvolatile memory devices.

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