

Electroluminescence from ZnCuInS/ZnS quantum dots/poly(9-vinylcarbazole) multilayer films with different thicknesses of quantum dot layer

Xiaofei Dong^a, Jianping Xu^a, Shaobo Shi^b, Xiaosong Zhang^a, Lan Li^{a,*}, Shougen Yin^{a,*}

^a Institute of Material Physics, Key Laboratory for Optoelectronic Materials and Devices of Tianjin, Key Laboratory of Display Materials and Photoelectric Devices of Ministry of Education, Tianjin University of Technology, Tianjin 300384, China

^b School of Science, Tianjin University of Technology and Education, Tianjin 300222, China

ARTICLE INFO

Keywords:

ZnCuInS/ZnS quantum dots
PVK polymer
Electroluminescence
Trap density

ABSTRACT

We report tunable electroluminescence (EL) from solution-processed ZnCuInS/ZnS (ZCIS/ZnS) quantum dots (QDs)/poly(9-vinylcarbazole) multilayer films. The EL spectra exhibit a red shift as the QD layer thickness increases. By analyzing the dependence of the applied voltage and the ZCIS/ZnS QD layer thickness on the EL spectra, the origin of the red shift is associated with the increased trap density of QDs that induces the injected electrons to be trapped in the deep donor level. The current conduction mechanism based on the current density–voltage curves at different voltage regions was discussed.

1. Introduction

High efficiency semiconductor quantum dots (QDs) have obvious potential applications in light-emitting diodes (LEDs) and displays [1,2]. Recently, eco-friendly ternary and quaternary compounds such as I–III–VI type QDs including CuInS₂ (CIS) [3], CuInSe [4], CuGaS₂ [5], and AgInS₂ [6], have drawn considerable attention owing to their large Stokes shift, high photoluminescence (PL) quantum yield, and size-tunable band gap in the visible region. The three ZnCuInS (ZCIS)/ZnSe/ZnS QD-based LEDs with red, yellow, and green electroluminescence (EL) emission bands were first reported by Xu's group in 2011 [7]. Recently, an external quantum efficiency (EQE) exceeding 7% was achieved in CIS QD-based LEDs with a CIS/ZnS heterostructure [8].

Most research has focused on engineering the device structure [9,10] and functionalizing QD surfaces to improve the performance of QD-based LEDs [11,12]. An appropriate functional layer is necessary for ensuring the charge carrier balance in the electroluminescent device. For example, optimizing the energy level of the organic hole-transport layer improved the EQE to 7.3% in the inverted-structured CdSe-based LEDs [13]. The performance of the CIS QD-based LEDs was obviously enhanced as the electron-transport layer of the ZnO film was replaced by the ZnMgO film [14]. The latter had an appropriate energy-band structure for the electron transport. Inserting poly(methylmethacrylate) (PMMA) between the CdSe QDs and the ZnO electron-transport layer improved the EL efficiency and the operational

stability in CdSe-based LEDs [9]. The insulating PMMA layer was considered to eliminate excess electrons and maintain the charge balance. A white emission with the Commission Internationale de l'Éclairage coordinates of (0.336, 0.339) in QD-LEDs was achieved by controlling the charge distribution through thickness modulation of the ZCIS/ZnS QDs and poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine) (poly-TPD) layers [15]. Surface engineering is an effective method to improve the device performance. The surface and defect states of QDs can influence the electron transfer and the electron trapping in QD-based LEDs. For CdSe-based LEDs, the charge injection efficiency was increased and the nonradiative recombination was suppressed by growing a graded and alloyed intermediate shell in CdSe QDs [1]. The ligand exchange on the surfaces of CIS QDs was carried out from long-chain oleylamine to short-chain 6-mercaptohexanol to increase the electron mobility within the CIS QDs and promoted the electron injection efficiency from the electron-transport layer to the CIS QD emitting layer in the multilayer structures of poly((9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-s-butylphenyl)diphenyl-amine) (TFB)/CIS QDs/ZnO [3].

The trap density is associated with the thickness of QD layer films, which can influence the scattering probability of the carriers and the carriers transport in the QD-based device [16]. In the present work, we fabricated ITO//PEDOT:PSS//poly(9-vinylcarbazole) (PVK)//ZCIS/ZnS QDs//Al multilayer films. The EL emission bands were found to be dependent on the thickness of QD layer films. The carrier transport

* Corresponding authors.

E-mail addresses: lilan@tjut.edu.cn (L. Li), sgyin@tjut.edu.cn (S. Yin).

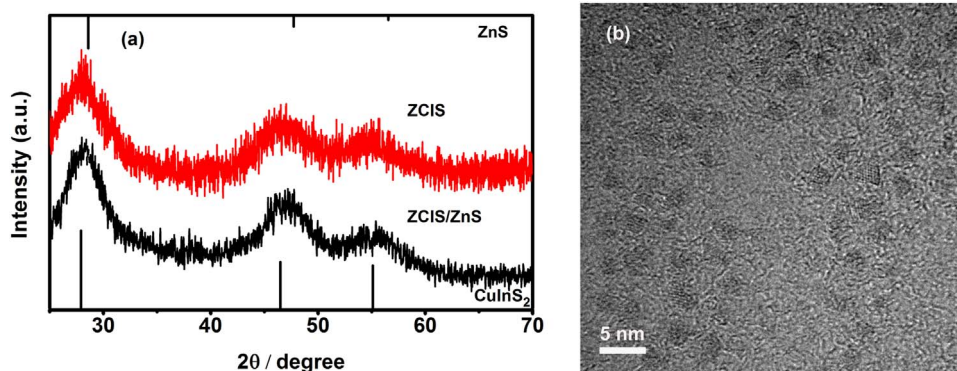


Fig. 1. (a) XRD patterns of ZCIS and ZCIS/ZnS QDs. (b) HRTEM image of ZCIS/ZnS QDs.

mechanism was discussed based on the device band structure and the current density–voltage (J – V) curve.

2. Experimental

2.1. Preparation of precursor solutions

Copper acetate ($\text{Cu}(\text{OAc})_2$, 99.99%), indium acetate ($\text{In}(\text{OAc})_3$, 99.99%), zinc acetate ($\text{Zn}(\text{OAc})_2$, 99.99%), sulfur powder (99.99%), dodecanethiol (DDT, 98.0%), octadecene (ODE, 90%), and oleylamine (OLA, 98.0%) were purchased from Aldrich. All chemicals were used without further purification.

A sulfur precursor solution was prepared by dissolving sulfur powder (0.4 mmol) into ODE (2.0 mL) at 120 °C under Ar flow. $\text{Zn}(\text{OAc})_2$ (0.2 mmol) was added into the mixture of OLA (1.0 mL) and ODE (2.0 mL) under the same reaction condition to form a clear zinc precursor solution. Two precursor solutions were stored at 50 °C for subsequent use.

2.2. Synthesis of ZCIS/ZnS QDs

The ZCIS/ZnS QDs were synthesized as in the previously reported method [17]. The synthesis reactions were all performed under Ar flow. $\text{Cu}(\text{OAc})_2$ (0.1 mmol), $\text{In}(\text{OAc})_3$ (0.4 mmol), and $\text{Zn}(\text{OAc})_2$ (0.1 mmol) were dissolved into a mixture solution of OLA (1.0 mL), DDT (1.0 mL), and ODE (6.0 mL). After degassing at 100 °C, the reactant was heated to 230 °C. The sulfur precursor solution was added into the solution and then stirred for 20 min to obtain ZCIS QDs. To grow a ZnS shell on the ZCIS QDs, after adding the sulfur precursor solution at 230 °C, the Zn precursor solution was added dropwise as the solution was heated to 240 °C. The reaction was maintained at 240 °C for 30 min to grow the ZnS shell. After being precipitated in excess acetone and purified by cosolvents of n-hexane and ethanol, the final production was dispersed into n-hexane for QD characterization and device fabrication.

2.3. Device fabrication

Devices with ITO//PEDOT:PSS//PVK//ZCIS/ZnS QDs//Al multilayer films were fabricated. The ITO glass substrates were cleaned in sequence by using liquid detergent, deionized water, acetone, isopropanol (isopropyl alcohol), and ethanol under ultrasonic agitation, followed by UV-ozone treatment for 15 min. The preparation process of multilayer films was as follows. First, 0.1 mL of PEDOT:PSS solution was spin-coated onto the ITO at 5000 rpm for 60 s and was heated in vacuum at 150 °C for 20 min. Then, 0.1 mL of PVK chloroform solution (3.0 mg/mL) was cast on top of the PEDOT:PSS layer at 3000 rpm for 30 s. This film was vacuum dried at 100 °C for 30 min. Subsequently, 0.1 mL of n-hexane dispersed QD solution was spin-coated on the surface of the PVK layer at 2000 rpm for 20 s several times, followed by the bake-off step at 80 °C for 60 min for each time. Finally, an Al

cathode with a thickness of 150 nm was thermally evaporated at a pressure of 6×10^{-4} Pa by a shadow mask with an active area of 4 mm². Three devices with different QD concentrations of 0.06, 0.2, and 1.0 mg/mL were fabricated and termed as A, B, and C.

2.4. Characterization

X-ray diffraction (XRD) measurements of ZCIS and ZCIS/ZnS QDs were performed by a Rigaku D/max 2500 v/pc diffractometer with Cu K α radiation. A high-resolution transmission electron microscopy (HRTEM) image of the ZCIS/ZnS QDs was obtained on a JEM-2100F transmission electron microscope. The absorption spectra of the ZCIS/ZnS QDs were characterized on a Hitachi UV-4100 UV–vis spectrophotometer. PL and EL spectra were measured by a Jobin Yvon FluoroLog-3 fluorescence spectrometer. A cross-sectional image of the multilayer films was obtained by using a field emission-scanning microscope (FE-SEM; Model SU-8010, Hitachi Japan). The thicknesses of QD films were measured with a profiler (AlphaStep D-100). For estimating the band gap of the QDs, the cyclic voltammetry (CV) measurement was performed in an electrolyte solution in which 0.1 M tetrabutylammonium perchlorate (TBAP) was dissolved in dichloromethane. A glassy carbon coated with a ZCIS/ZnS QD n-hexane solution was used as the working electrode. A Pt wire and Ag/AgCl were selected as the counter electrode and reference electrode, respectively. The J – V curves were measured by using a Keithley 2400 source meter.

3. Results and discussion

A cubic zinc blende structure of ZCIS QDs was identified from the XRD patterns in Fig. 1(a) in which the three main diffraction peaks are located between CuInS_2 (JCPDS 85-1575) and ZnS (JCPDS 65-9585) [18]. It can be noted that all the diffraction peaks evidently shift to large angles after ZnS shell deposition and approach the characteristic peaks of bulk ZnS. The average diameter of the ZCIS/ZnS QDs was 2.9 nm as determined by HRTEM, shown in Fig. 1(b). The unrecognized core/shell structure is considered to have a very thin shell thickness, and this is similar to the results obtained by some research groups [19,20].

The PL spectra of ZCIS and ZCIS/ZnS QDs when excited at 380 nm are shown in Fig. 2. Both the QDs exhibit a broad visible emission band. After ZnS is deposited, the emission band of the ZCIS QDs is blue shift from 635 to 586 nm, and this is in agreement with the findings of the work of Kim et al. [20]. This is attributed to the increase in the band gap because of the surface cation exchange between $\text{Cu}^+/\text{In}^{3+}$ and Zn^{2+} . Moreover, the emission intensity of ZCIS/ZnS QDs increase significantly with a decrease in the nonradiative transition probability.

The energy level structure of the ZCIS/ZnS QDs was determined by the absorption spectrum [Fig. 3(a)] and the CV measurement [Fig. 3(b)]. The optical band gap (E_g) value was estimated as 2.52 eV

Download English Version:

<https://daneshyari.com/en/article/5447452>

Download Persian Version:

<https://daneshyari.com/article/5447452>

[Daneshyari.com](https://daneshyari.com)