Green Electroluminescence Generated by Band-edge Transition in Ag-In-Ga-S/GaS_x Core/shell Quantum Dots

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Abstract Quantum-dot light-emitting diodes (QD-LEDs) that exhibit green emission were fabricated using Ag-In-Ga-S/GaS_x (AIGS) core/shell QDs as low-toxicity QDs. Although multi-element QDs such as AIGS are prone to broad-wavelength defect-induced emission, the core/shell structure enables sharp emission from band-edge transitions. The electroluminescence (EL) spectra were found to include a large defect emission component compared with the photoluminescence spectra of the QD films because of the difference in the excitation process of the QDs. The defect emission was attributed to the electrons injected into the emitting layer (EML) being easily trapped at the defect sites in the QDs. The addition of an electron transporting material to the EML effectively blocked the direct injection route and reduced the electron trapping at the defect sites. Consequently, the color purity of the EL emission was enhanced and the QD-LEDs exhibited green EL emission.

Keywords: Quantum dot, Light-emitting diode, Electroluminescence, Band edge emission, Defect emission, Chalcopyrite-type QD.

1. Introduction

Ultra-high-definition television systems have been researched and developed to realize television services that provide realistic visuals. The video format (ITU-R recommendation BT.2020) defines not only the number of pixels but also a wide-color-gamut color system. The wide color gamut of ultra-high-definition television systems, which enables them to express a wider range of colors than a conventional high-definition television, requires red, green, and blue primary colors with extremely high color purity.¹⁾ Realizing pure-green emission is particularly difficult because the full-width at half-maximum (FWHM) must be extremely narrow.

As a light-emitting material for realizing wide-color-gamut displays, quantum dots (QDs) that emit light with high color purity have attracted attention. A QD is a semiconductor nanocrystal that exhibits a quantum size effect in which the energy state changes when electrons

are confined in a narrow region. The optical bandgap of QDs can be tuned by controlling the size of the core.²⁾ Notably, the photoluminescence (PL) spectra of QDs are very narrow when their size distribution is narrow.

Therefore, QDs are suitable for use in wide-color-gamut displays. The application of QDs to electroluminescence (EL) devices has been studied.³⁾ QD light-emitting diodes (QD-LEDs) with a QD film as an emitting layer (EML) enable the fabrication of thin, lightweight, and flexible displays with a wide color gamut and high image quality. Because QD-LEDs can be manufactured via the coating process, they are also expected to reduce the manufacturing cost for larger screens.

Several QD-LEDs based on CdSe QDs have been reported.⁴⁾⁻⁸⁾ Although these Cd-based QD-LEDs show emission with a narrow FWHM and high efficiency, the toxicity of Cd remains an unsolved problem. Researchers have thus attempted to fabricate QD-LEDs with low-toxicity QDs. InP QDs are one of the substitutes for Cd-based QDs. In conjunction with advances in the device structure and QD structure, the performance of QD-LEDs fabricated using InP-based QDs has been improved.⁹⁾⁻¹⁴⁾ However, the luminous efficiency and color purity of InP-based QD-LEDs remain inferior to those of Cd-based ones.

Chalcopyrite-type QDs composed of I-III-VI₂-group

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elements have been investigated.¹⁵⁻¹⁷ These QDs are promising luminescent materials because they are direct-transition semiconductors and are composed of low-toxicity elements. The bandgaps of solid-solution nanoparticles (NPs) of AgInS₂-AgGaS₂¹⁶ and AgInS₂-ZnS¹⁷ can be tuned by manipulating either their Zn or Ga content or their particle size. QD-LEDs with AgInS₂-based NPs have been reported.¹⁸⁻²⁰ However, their emission spectra are much broader than those of Cd-based or InP-based QDs because of emission originating at lattice defect sites.

Recently, chalcopyrite-type QDs have been reported to generate intense, spectrally narrow PL from a band-edge transition.²¹ Although AgInS₂ QDs exhibit a broad PL peak, AgInS₂/GaS_x core/shell QDs exhibit an intense narrow PL peak. Furthermore, Ag-In-Ga-S/GaS_x (AIGS) core/shell QDs, which include solid-solution NPs of Ag-In-S and Ag-Ga-S with a GaS_x shell, exhibit band-edge emission, the wavelength of which is tunable in the visible-light wavelength region.²² These findings indicate that AIGS core/shell QDs are a promising candidate material for QD-LEDs.

In our previous study on the EL of QD-LEDs with AgInS₂/GaS_x core/shell QDs, we achieved yellow EL emission that was mainly composed of band-edge emission.²³ The results indicated that the EL of QDs with defect sites would exhibit a different emission spectrum from that of PL. We found that identifying an appropriate QD for use in QD-LEDs required an EL evaluation for each type of QD.

In the present paper, we fabricated QD-LEDs using AIGS core/shell QDs that exhibit vivid green PL emission and investigated their EL properties. Although the fabricated QD-LEDs exhibited emission that included a broad defect-induced component and a sharp band-edge component, the defect-induced component was effectively suppressed by the improvement of the electron injection process into the QDs. Consequently, the color purity of the EL emission was enhanced and QD-LEDs fabricated using AIGS core/shell QDs were observed to exhibit green EL emission.

2. Experimental

2.1 Synthesis of AIGS core/shell QDs

AIGS core/shell QDs were synthesized using the previously reported method.²² Elemental sulfur powder (0.23 mmol), which served as an S²⁻ precursor, and a mixture of silver acetate (0.083 mmol), gallium acetylacetonate (0.075 mmol), and indium acetylacetonate (0.05 mmol),

which was used as metal-ion precursor, were placed in a test tube. After a mixture of oleylamine (2.75 mL) and 1-dodecanethiol (0.25 mL) was added, the resultant solution was heated at 300 °C for 10 min with vigorous stirring under a N₂ atmosphere. Large particles were removed by centrifugation, and AIGS core QDs were precipitated by the addition of excess methanol. Ten nanomoles (in terms of NPs) of AIGS core QDs were dispersed in chloroform and mixed with a gallium acetylacetonate (0.053 mmol) and thiourea (0.053 mmol) suspension in oleylamine (3.0 mL). The mixture was subsequently heated to 300 °C for 15 min. The obtained AIGS core/shell QDs were washed several times with methanol and ethanol and uniformly dissolved in chloroform.

2.2 Fabrication of QD-LEDs

Glass substrates, onto which a 100-nm-thick indium tin oxide (ITO) cathode was deposited and patterned, were degreased via sequential sonication in a detergent solution and ethanol, followed by further treatment using an ultraviolet-ozone cleaner. A 40-nm-thick layer of ZnO NPs, which functioned as the electron injection layer (EIL), was formed by spin-coating from a 1-butanol dispersion prepared in accordance with a previously reported method.⁵ The AIGS core/shell QD concentration was fixed at 2.3 mg mL⁻¹ in chloroform, and tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB),²⁴ as an electron-transporting material (ETM), was added to the dispersions to yield QD:3TPYMB = 1:1.3 by weight. The QD dispersions for EMLs were spin-coated onto the EIL. The QD-LED without 3TPYMB had a QD EML approximately 10 nm thick. The thickness of the EMLs mixed with 3TPYMB varied depending on the amount of 3TPYMB. When the mixing ratio of QD and 3TPYMB was 1:1.3, the thickness was approximately 35 nm. The substrates were then loaded into a vacuum deposition chamber, and a 30-nm-thick hole-transport layer (HTL, consisting of tris(4-carbazoyl-9-ylphenyl) amine (TCTA)), a 10-nm-thick hole injection layer (HIL) composed of MoO₃, and an 80-nm-thick Al anode were deposited. The devices were encapsulated with a glass cap under a N₂ atmosphere.

3. Results and discussion

3.1 PL characteristics of AIGS core/shell QDs

Fig. 1 shows the PL spectra of the synthesized AIGS core/shell QDs dispersed in chloroform and those embedded in a spin-coated film. The QD dispersion exhibited green PL with an intense sharp peak at ~539 nm and a broad shoulder at wavelengths longer than 600 nm. The appearance of a sharp peak derived from a

Fig.1 PL spectra of synthesized AIGS core/shell QDs dispersed in chloroform and an AIGS core/shell QD film. The inset shows a photograph of an AIGS core/shell QD dispersion under UV light.

band-edge transition implies that the GaS_x shell effectively suppressed surface defects.²¹⁾²²⁾ The FWHM value was 36 and 39 nm for the dispersion and the film, respectively. The PL spectra of the film tended to spread to the longer-wavelength side compared to the dispersion. It is considered that the excitation energy in the film is more easily transferred to larger nanocrystals or defect sites which have lower energy levels. The PLQY of the dispersion was 10.1%.

3.2 EL spectra from AIGS core/shell QDs

Fig. 2(a) shows the structure of the QD-LED with an EML consisting of only the AIGS core/shell QDs. Fig. 2(b) shows the EL spectra recorded under two luminance conditions, where the intensity was normalized with respect to the peak wavelength of the sharp band-edge emission. The inset photograph of the AIGS QD-LEDs at approximately 1 cd m^{-2} shows yellow EL with some bright spots due to the nonuniformity of the QD layer. The EL peaks in the wavelength region from 600 to 800 nm, which are considered to be derived from defect sites, are much more intense than those in the PL spectrum of the QD film (Fig. 1).

The intensity ratio of defect emission to band-edge emission in the EL spectra at 3.1 cd m^{-2} was lower than that at 0.04 cd m^{-2} . This difference in the intensity ratio of defect emission to band-edge emission between EL and PL suggests the existence of specific defect sites at the interface between the GaS_x shell and AIGS core. If such defect sites accept externally injected electrons or holes more easily than their photogenerated counterparts, the ratio of defect emission in the EL spectra will be higher than that in the PL spectra. Even if such defect sites exist, the probability of the carriers becoming trapped in them would change depending on the electric field. In addition, the carriers are more easily injected into the

Fig.2 (a) Structure of a QD-LED with an EML consisting of only AIGS core/shell QDs. (b) EL spectra of the QD-LED for two values of luminance. The inset shows a photograph of the EL from the QD-LED at approximately 1 cd m^{-2} .

conduction or valence bands because defect sites are filled as the injection rate increases. This easier carrier injection might explain why the intensity ratio of defect emission to band-edge emission at 3.1 cd m^{-2} was lower than that at 0.04 cd m^{-2} .

3.3 Suppression of defect emission by mixing ETM into QDs

To suppress the defect emission, we added 3TPYMB as an ETM into the QD film, as schematically shown in Fig. 3(a). The EML was spin-coated from chloroform solutions containing QDs and 3TPYMB with a mixing ratio of 1:1.3 by weight. The addition of ETM effectively suppressed defect emission, as shown in Fig. 3(b). The inset photograph shows the EL from the QD-LEDs at approximately 1 cd m^{-2} ; it is greener than that shown in Fig. 2(b) and uniform.

Fig. 3(c) shows the chromaticity variation according to the luminance of QD-LEDs with and without 3TPYMB in the International Commission on Illumination (CIE) 1931 color space. The chromaticity of the QD-LED without 3TPYMB exhibited a large change from (0.491, 0.502) to (0.422, 0.566) with increasing luminance, whereas that with 3TPYMB exhibited only a slight change from (0.388, 0.596) to (0.390, 0.584). Although the chromaticity of EL in the QD-LED with 3TPYMB is not as good as the chromaticity of the PL in the QD film—specifically, (0.340, 0.635)—it is greatly improved compared with that of the QD-LED without 3TPYMB.

3.4 EL characteristics of QD-LEDs and the layer state of EML mixed with ETM

The current density-applied voltage and luminance-applied voltage curves for the QD-LEDs without and with 3TPYMB incorporated into their EML are shown in Fig. 4(a). The turn-on voltage of the QD-LED with

Fig.3 (a) Structure of a QD-LED with an EML containing QDs mixed with 3TPYMB. (b) EL spectra of the QD-LED with 3TPYMB for two values of luminance; the inset shows a photograph of the EL from the QD-LED at approximately 1 cd m⁻². (c) Chromaticity variation according to the luminance of QD-LEDs without and with 3TPYMB in the CIE 1931 color space.

Fig.4 (a) Current density–applied voltage and luminance–applied voltage plots for AIGS QD-LEDs without and with 3TPYMB in the EML. (b) Cross-sectional STEM image of a typical QD-LED with a mixed EML of QDs and 3TPYMB (mixing ratio: 1:2) and an enlarged view of the EML. (c) Energy levels of the materials used in the QD-LEDs.

3TPYMB was ~3.6 V, whereas that of the QD-LED without 3TPYMB was ~2.0 V. This substantial increase in the turn-on voltage indicates that the electron injection through 3TPYMB was difficult compared with the direct injection from the ZnO EIL.

The relationship between the deposition state of the mixed EML and the EL characteristics is described. Fig. 4(b) shows a cross-sectional scanning transmission electron microscopy (STEM) image of a typical QD-LED with a mixed EML of AIGS core/shell QDs and 3TPYMB (mixing ratio: 1:2). The cross-sectional STEM images were obtained with a scanning electron microscope (Hitachi High-Tech S-5500) after cross-sectional processing using focused ion beam. Each layer can be distinguished, revealing that an appropriate layered structure was obtained. However, the QDs and 3TPYMB were not uniformly dispersed in the EML. Most of the QDs were located at the upper side of the EML, leaving 3TPYMB at the lower side. The QDs were coated with an alkyl-chain compound, which has a low surface

energy,²⁵⁾ and polar molecules tended to phase-separate when the solvent was drying during the coating process.¹³⁾¹⁴⁾²⁶⁾

The results suggest that the lower part of the mixed EML functions as an electron transport layer (ETL) and that the upper, QD-rich part, emits EL. Fig. 4(c) shows the energy levels of each material used in the present study. The valence-band energy level (E_{VB}) of the QDs was measured by photoelectron spectroscopy (AC-3), and the conduction-band energy level (E_{CB}) was calculated from the E_{VB} and the bandgap estimated from the energy at the absorption edge. The E_{VB} and E_{CB} of the ZnO NPs,⁵⁾²⁷⁾ as well as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of 3TPYMB²⁴⁾ and TCTA²⁸⁾²⁹⁾, were taken from the literature. The LUMO energy level of 3TPYMB is similar to the E_{CB} of the QDs; thus, electron injection from 3TPYMB to the QDs is feasible. However, because the HOMO energy level of 3TPYMB is lower than the E_{VB} of the QDs and the HOMO of TCTA

(an HTL), holes are not easily injected from the TCTA into 3TPYMB but are injected smoothly into the QDs. The 3TPYMB, without being excited, acts as both an ETL and a hole blocking layer (HBL).

Because the addition of ETM suppressed defect emission, we speculate that specific defect sites enable electrons to pass around the conduction band edge of the AIGS core. For the device fabricated without 3TPYMB, an electron injection barrier of approximately 0.7 eV was observed for the AIGS core/shell QD layer; the electrons that could not cross the injection barrier were more likely to be injected into the defect levels. However, when the QDs were mixed in 3TPYMB and the direct injection route for the electrons was blocked, the number of electrons trapped by injection into the QDs likely decreased, whereas the turn-on voltage of the QD-LEDs increased. Therefore, the excitation process of the QDs was modified to reduce the electron trapping, which led to suppression of the defect emission. For further improvement of the EL characteristics, the GaS_x shell should be modified to improve the PLQY of the AIGS core/shell QD film. Furthermore, the structure of the QD-LEDs should be optimized by selecting peripheral materials that match the AIGS core/shell QDs.

4. Conclusion

We investigated the EL characteristics of QD-LEDs fabricated using AIGS core/shell QDs with green band-edge emission. EL emission mainly composed of band-edge emission was observed for the AIGS-based QD-LEDs. However, the EL spectra of the QD-LEDs included a large defect emission component compared with the PL spectra of the QD film because of the difference in the excitation process of the QDs. This defect emission was attributed to the electrons injected into the EML being easily trapped at the defect sites in the QDs. Mixing 3TPYMB as an ETM into the EML blocked the direct injection route for the electrons. The excitation process of the QDs was modified to reduce the electron trapping, which led to suppression of the defect emission. Consequently, the color purity of the EL emission was enhanced and the QD-LEDs fabricated using AIGS core/shell QDs exhibited green EL emission. We hope that the proposed method of improving the EL characteristics will contribute to the development of high-color-purity displays with QD-LEDs that do not contain toxic materials.

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