Green Light-emitting Diodes Using Ag-In-Ga-S/GaS_x Quantum Dots with Narrow Spectral Bandwidth

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Keywords: Quantum dot, Electroluminescence, Light-emitting diode, Spectrum, I−III−VI_2 semiconductor

ABSTRACT

Light-emitting diodes fabricated using Ag-In-Ga-S/GaS_x quantum dots that exhibit vivid green emission were investigated, along with their electroluminescence (EL) properties. Defect-related emission components in the EL spectrum were suppressed by treatment with Ga compounds, and the EL exhibited color purity comparable to the photoluminescence.

1 Introduction

Colloidal quantum dots (QDs) have attracted attention as light-emitting elements for realizing a wide-color-gamut display because of their narrow spectral bandwidth, which causes high color saturation. The wide color gamut of ultra-high-definition television systems, defined in Recommendation ITU-R BT. 2020, requires red, green, and blue primary colors with extremely high color purity. Although green chromaticity strongly affects the gamut of a display, realizing pure green emission is particularly difficult because the full width at half-maximum (FWHM) must be extremely small.

QDs are semiconductor nanocrystals with sizes on the order of several nanometers, and the optical bandgap of QDs can be tuned by controlling the size and the chemical composition of the core. Applications related to the electroluminescence (EL) of QDs have also been studied. QD light-emitting diodes (QD-LEDs) enable the fabrication of thin, lightweight, and flexible displays with a wide color gamut and high image quality.

Although Cd-based QD-LEDs show emission with a small FWHM and high efficiency, the toxicity of Cd remains a problem.[1,2] InP QDs are a substitute for Cd-based QDs.[3,4] However, the luminous efficiency and color purity of green-emitting InP-based QD-LEDs are inferior to those of Cd-based QD-LEDs.

QDs composed of I−III−VI_2 semiconductors have also attracted intensive attention for possible applications in various photofunctional devices.[5,6] QD-LEDs with $AgInS_2$- and $CuInS_2$-based QDs have been reported.[7-9] These QD-LEDs show broad EL spectra derived from the QDs. Recently, $AgInS_2$-based QDs have been reported to generate intense, spectrally narrow PL associated with a band-edge transition. Although $AgInS_2$ core QDs exhibit a broad PL peak, $AgInS_2/GaS_x$ core/shell QDs exhibit an intense narrow PL peak.[10] In addition, Ag-In-Ga-S/GaS_x core/shell QDs (AIGS QDs) exhibit band-edge emission, the wavelength of which is tunable in the visible-light wavelength region.[11] AIGS QDs with adjusted composition emit vivid green luminescence. The FWHM of 32 nm is smaller than that for other Cd-free QDs.[12,13] These findings indicate that AIGS QDs are promising candidates for QD-LEDs.

In our previous study on the EL of QD-LEDs, we reduced defect-related emission by adding an electron-transporting material (ETM) to the emitting layer (EML).[14,15] However, the broad EL component derived from defect sites was more intense than the PL emission from the QD film.[15] This defect-related emission must be suppressed in order to achieve sufficient color purity for AIGS QDs to be utilized in QD-LEDs.

In the present study, we synthesized AIGS QDs that exhibit vivid green PL emission, and fabricated QD-LEDs using the AIGS QDs. The defect-related emission components in the EL spectrum were suppressed by treatment with Ga compounds, and the EL exhibited a color purity comparable to that for PL from a AIGS QD film. Thus, low-toxicity QDs that emit green EL with high color purity and an extremely narrow FWHM were achieved.

2 Experiment

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 ZnMgO nanoparticles, which functioned as the electron injection layer (EIL), was deposited by spin-coating from an ethanol dispersion and subsequently baked at 180 °C. ZnMgO nanoparticles were prepared according to a previously reported method.[16] For some QD-LEDs, $GaCl_3$ was spin-coated onto ZnMgO EIL from a chloroform solution and baked at 210 °C. AIGS QDs

were synthesized using a previously reported method.[12,13] The synthesized AIGS QDs were washed several times and uniformly dissolved in chloroform. The AIGS QD concentration was fixed at 1.8 mg m^{-1}, and tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB), as an ETM, was added to the dispersions to yield QD:3TPYMB = 1:0.8 by weight. For some QD-LEDs, $GaCl_3$ and $Ga(DDTC)_3$ were also added to the dispersions to yield QD:3TPYMB: $GaCl_3$:$Ga(DDTC)_3$ = 1:0.8:0.05:0.05 by weight. The QD dispersions for EMLs were spin-coated onto the EIL and baked at 100 °C. The thickness of the mixed EML was approximately 15 nm. The substrates were then loaded into a vacuum deposition chamber, and a 40-nm-thick hole-transport layer (HTL) of tris(4-carbazoyl-9-ylphenyl) amine (TCTA), a 10-nm-thick hole-injection layer (HIL) of MoO_3, and an 80-nm-thick Al anode were deposited. The devices were encapsulated with a glass cap under a N_2 atmosphere.

3 Results and Discussion

3.1 PL characteristics of AIGS QDs

Fig. 1(a) shows PL spectra normalized by the emission peak intensity of the synthesized AIGS QDs prepared as a dispersion in chloroform and as a spin-coated film. Fig. 1(b) shows the chromaticity of the PL from the AIGS QDs in the dispersion and the film states according to the International Commission on Illumination (CIE) 1931 color space. The QD dispersion exhibited green PL with an intense sharp peak at a wavelength of 529 nm and a slight broad shoulder at wavelengths longer than 580 nm. The appearance of a sharp peak derived from band-edge transitions implies that the GaS_x shell effectively suppressed surface defects.[10] The FWHM of the PL spectra observed from the AIGS QDs was 32 nm, which is extremely small for emission from low-toxicity QDs.

The AIGS QD film exhibited PL with a peak at a wavelength of 532 nm and with a FWHM of 32 nm; the photoluminescence quantum yield (PLQY) was 16%. The chromaticity coordinates of the green PL changed from (0.236, 0.709) in the dispersion to (0.271, 0.676) in the film. The peaks in the PL spectra of the film tended to shift to the longer wavelength compared with the peaks in the PL spectra of the dispersion. We speculated that the excitation energy in the film is more easily transferred to larger nanocrystals or defect sites with lower energy levels.

The EML was formed by mixing AIGS QDs, 3TPYMB, and Ga compounds consisting of $GaCl_3$ and $Ga(DDTC)_3$ to enhance the luminescence properties. Table 1 shows the PLQY and chromaticity for the films prepared under different conditions. The mixing ratio for the mixed EML was QD:3TPYMB:Ga compounds = 1:1:0.1 by weight. Although the PLQY was not improved, the incorporation of 3TPYMB slightly suppressed defect-related emission in the spectra. The addition of Ga compounds to the EML led to an increase in the PLQY. Although these Ga compounds increased the PLQY when added individually, the combination of $Ga(DDTC)_3$ and $GaCl_3$ at a 1:1 weight ratio increased the PLQY to 32%.

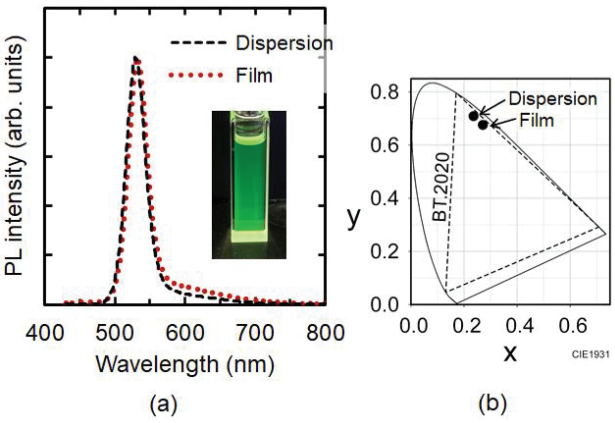

Fig. 1 (a) PL spectra of synthesized AIGS QDs as a dispersion in chloroform and as a spin-coated film. The inset shows a photograph of an AIGS QD dispersion under UV light. (b) Chromaticity of the PL of the AIGS QDs in the CIE 1931 color space.

Table 1 PLQY and chromaticity of AIGS QD films prepared under different conditions.

Film conditions	PLQY	Chromaticity coordinates
QD-only	16	(0.271, 0.676)
QD+3TPYMB	15	(0.259, 0.696)
QD+3TPYMB+ $GaCl_3$	27	(0.255, 0.699)
QD+3TPYMB+ $GaCl_3$+$Ga(DDTC)_3$	32	(0.262, 0.697)
QD+3TPYMB+ $Ga(DDTC)_3$	25	(0.261, 0.697)

3.2 EL spectra of QD-LEDs with mixed EMLs

Fig. 2(a) shows the structure of a QD-LED with an EML consisting of AIGS QDs. EMLs were prepared under three conditions: QD-only, QD+3TPYMB, and QD+3TPYMB+Ga compounds. Fig. 2(b) shows the EL spectra of the QD-LEDs at low luminance (0.01 cd m^{-2}) for the three EMLs, where the intensity was normalized with respect to the peak wavelength of the sharp band-edge emission. The EL intensity in the wavelength region from 600 to 800 nm, which is strongly observed in

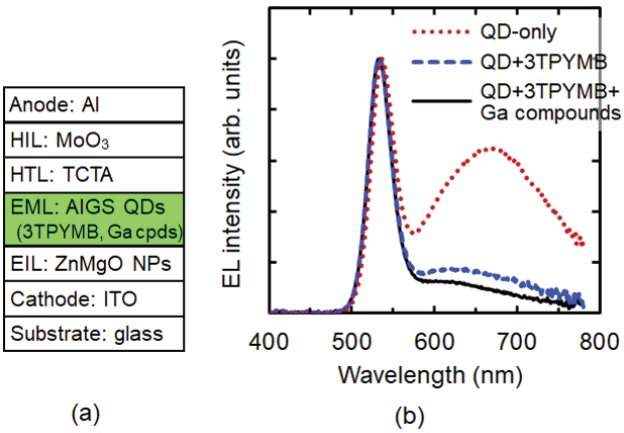

Fig. 2 (a) Device structure of QD-LEDs and (b) EL spectra of the QD-LEDs with three different EMLs, as recorded at low luminance (0.01 cd m^{-2}).

the QD-only EML, is much more intense than that in the PL spectrum of the QD film. Because the QD-LEDs do not contain materials that emit in the wavelength range 600–800 nm, the peak was attributed to an intensification of the defect-related emission component for the AIGS QDs. When the QDs were excited through injection of electrons and holes under an applied electric field, the carriers were easily injected into defect sites with low energy barriers and the luminescence generated by these sites was accentuated. Although the EL spectra at low luminance were improved by the incorporation of 3TPYMB and Ga compounds, the defect-related emission component was still larger than that for PL. The defect-related emission components for each QD-LED were reduced with increasing luminance, and the EL spectra of the QD-LEDs with the mixed EMLs were similar to the PL spectrum. However, the problem remained that the spectra varied depending on the luminance.

3.3 $GaCl_3$ treatment of the ZnMgO EIL

The EL spectra of the QD-LEDs can be improved by suppressing direct injection into defect sites during electron injection from a ZnMgO EIL into the AIGS QDs. The conduction band of ZnMgO can be shifted to higher energy when the surface of the ZnMgO NPs is treated with Cl.[17] We carried out a Cl treatment by spin-coating a chloroform solution of $GaCl_3$ onto the ZnMgO EILs. The coated $GaCl_3$ was not only deposited onto the EIL surface, but also penetrated into the EIL.

Fig. 3(a) shows current density–applied voltage and luminance–applied voltage curves for QD-LEDs with the mixed EML on the EILs treated with $GaCl_3$. Because $GaCl_3$ treatment reduces the electron injection into the AIGS QDs, a treatment-adjusted amount of $GaCl_3$ was applied to keep the turn-on voltage below 2.5 V. Fig. 3(b) shows the EL spectra of QD-LEDs at low luminance (0.01 cd m^{-2}) and high luminance (175 cd m^{-2}). The spectra have approximately the same shape as the PL spectrum, where the FWHM remained at 33 nm and almost no change was observed in the EL spectra depending on the luminance. Fig. 3(c) shows the chromaticity of the EL from the QD-LEDs and the PL from the mixed QD film in the CIE 1931 color space. The chromaticity of the QD-LEDs exhibited only a slight change from (0.268, 0.689) to (0.260, 0.695) in the luminance range from 0.01 to 175 cd m^{-2}, which is almost identical to the chromaticity coordinates for the PL from the AIGS QD film (0.262, 0.697).

4 Conclusions

AIGS QDs composed of group I–III–VI_2 elements were synthesized and exhibited vivid green PL emission with an intense sharp peak with a FWHM of 32 nm. In addition, QD-LEDs fabricated using AIGS QDs were investigated, along with their EL properties. The EL

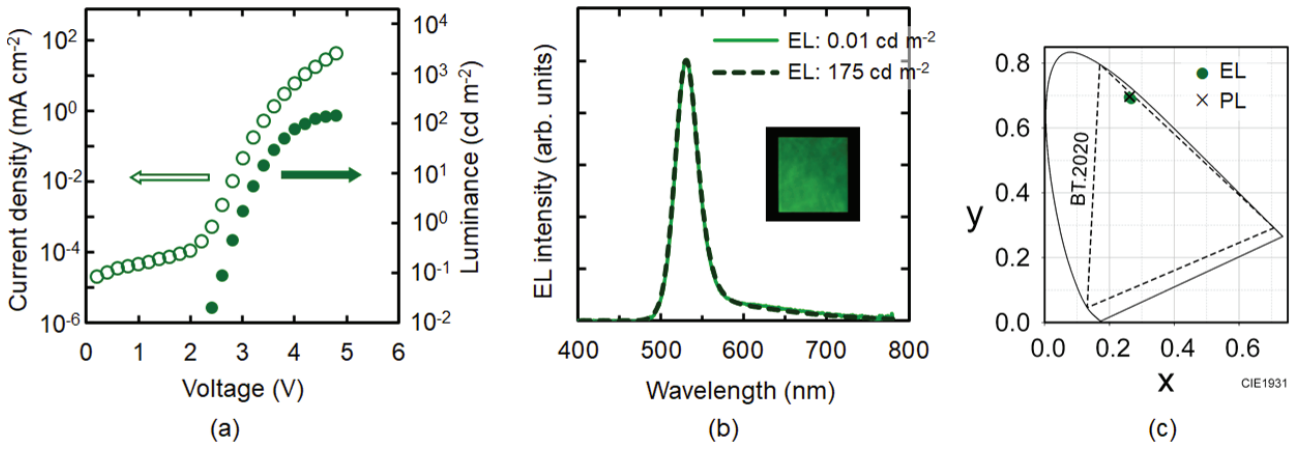

Fig. 3 (a) Current density–applied voltage and luminance–applied voltage plots for AIGS QD-LEDs with mixed EML on EILs treated with $GaCl_3$. (b) EL spectra of QD-LEDs at low luminance (0.01 cd m^{-2}) and at higher luminance (175 cd m^{-2}). (c) Chromaticity of EL from QD-LEDs and PL from mixed QD film.

spectra of the AIGS QD-LEDs were found to include a larger defect-related emission component than the PL spectra of AIGS QD films. Therefore, AIGS QDs were treated with Ga compounds such as $GaCl_3$ and $Ga(DDTC)_3$, and the ZnMgO EILs were also treated with $GaCl_3$. As a result, the defect emission components in the EL spectra were suppressed and the EL characteristics were enhanced. The EL with a FWHM of 33 nm exhibited a color purity comparable to that for the PL from the AIGS QD film without exhibiting a luminance dependence.

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