Highly Efficient (Infra)-Red-Conversion of InGaN Light Emitting Diodes by Nanocrystals, Enhanced by Color Selective Mirrors

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Colloidal nanocrystal layers deposited onto the enclosure of InGaN light emitting diodes are demonstrated to operate as nano-phosphors for color conversion with high color stability. Dependent on the choice of the nanocrystal materials, either CdSe/ZnS or PbS nanocrystals are applied, the diode emission at 470 nm is converted to the red or to infrared light, with similar quantum efficiencies. The color conversion is further improved by dielectric mirrors with high reflectivity at the emission band of the nanocrystals, resulting in an almost doubling of the nanocrystal light extraction from the devices, which increases the nanocrystal device efficiency up to 19.1%.

Introduction

The development of energy and cost efficient, reliable and long-lived solid state light emitting devices with excellent color stability and color rendering capability is one of the main challenges in lighting industry [1] – [3]. As a result of the continuing progress in the development of solid state light sources for more and more applications incandescent or fluorescent light sources are replaced by light emitting diodes [1], [2] (LEDs) based on III-V nitride compound semiconductors. These LEDs emit in the blue or in the blue-green [4] and color conversion with phosphors is commercially adopted to generate “white” light from a single-chip LED by combining the converted light, i.e. the phosphor emission with the remaining blue LED emission [1]. Promising candidates to be used as nano-phosphors are in particular CdSe/ZnS core/shell nanocrystals (NCs) due to their excellent environmental stability combined with their exceedingly high fluorescence quantum yield [5]. While in the previous reports the excellent color quality of nanocrystal based color conversion has been highlighted [6], here we rather focus on the efficiency of the color conversion, which we almost double by depositing color selective Bragg mirrors directly onto the LED devices. By controlling the film thickness of the nanocrystals on the InGaN LEDs, light emission ranging from blue to pure red is demonstrated with excellent brightness dependent color stability. Furthermore, color conversion from the blue to the near-infrared spectral region is demonstrated by using PbS NCs, resulting in as high quantum efficiencies as in the visible.

Sample Preparation

For the color conversion experiments we make use of commercial InGaN-LEDs (Nichia corporation, type NSPBF50S) exhibiting strong blue electroluminescence around a wavelength of 470 nm, and having a molded and transparent epoxy enclosure with a flat-top surface. Onto the flat surface uniform films of colloidal CdSe/ZnS core/shell

NCs in a polymethyl methacrylate (PMMA) matrix are deposited by drop- or spin-casting, depending on the required NC-quantity (sample series S1). The NC volume fraction amounts 2.53% corresponding to a NC density n_{NCs}=4.37x10^{17} cm^{-3}. The total number of deposited NCs is varied between 6.54x10^{11} and 1.97x10^{14}. Prior to the mixing into the PMMA, dodecylamine (DDA) is added to the NCs delivered from NFM Ltd (m_{NCs}:m_{DDA} = 2:1) to improve their surface passivation and their dispersion in chlorobenzene (CB). An image of a diode with a NC film deposited on its oval shaped surface (length 4 mm and width 1.8 mm) is shown in the inset in Fig 1 (b). We have made use of two series of samples, for the series S1 the NCs are directly deposited on the enclosure of the LEDs, while for the series S2 a Bragg interference mirror was placed underneath the NC layer, to recycle photons emitted back into the device.

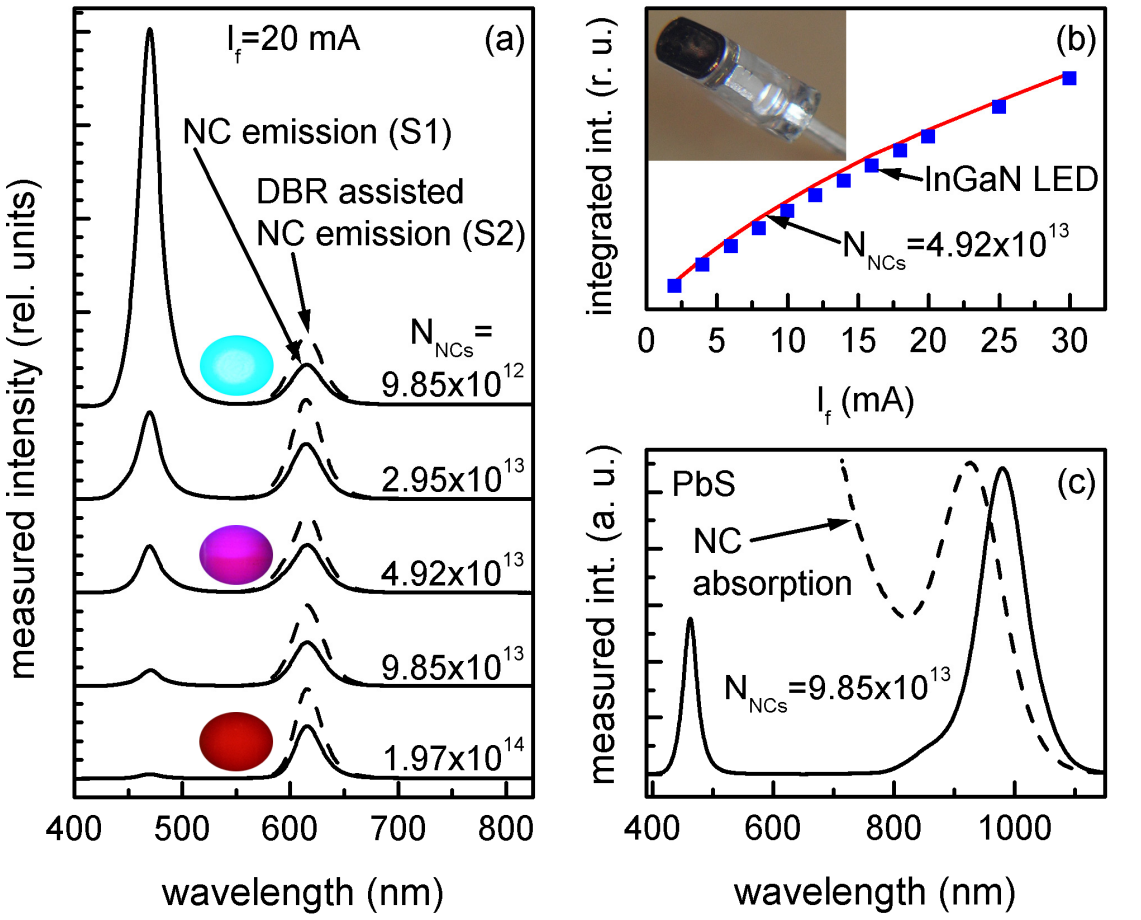

Fig. 1: (a) Emission spectra from sample series S1 (solid lines) and S2 (dashed lines) for different deposited nanocrystal quantities (N_{NCs}). For 9.85x10^{12}, 4.92x10^{13} and 1.97x10^{14} nanocrystals, respectively, the color of the emission is given by the photographs taken from the top of the devices. (b) Spectrally integrated InGaN (squares) and nanocrystal emission (solid line) as function of the LED forward current. The inset shows a photograph of the device with a PbS-PMMA film deposited on top. (c) Absorption spectrum (dashed line) of PbS nanocrystals in solution, used as active material for near-IR color conversion. Emission spectrum (solid line) of a PbS-LED device covered by 9.85x10^{13} nanocrystals.

Conversion Results

For the optical characterization all side faces of the LED enclosure are carefully covered by a black tape to detect emission from the NC covered areas only. The spectra were measured by collecting a part of the hemispherical emission of the devices. To determine the conversion efficiencies, a calibrated photodiode with a flat spectral response was used. The color conversion is demonstrated in Fig. 1 (a), showing the emission spectra of the devices from series S1 biased by a forward current of 20 mA. For clarity, the spectra of samples covered by different NC quantities are shifted in vertical direction with respect to each other. The spectra show clearly two emission maxima, one around 470 nm corresponding to the emission generated in the InGaN diode and the second one around 615 nm originating from the NC film deposited on top of the diode enclosure. With increasing quantity of deposited NCs the intensity of the direct emission from the LED decreases whereas the emission from the NCs slightly increases. By controlling the intensity ratio between the LED and the NC emission the color of the device is tuned between light blue, observed for a NC amount of 9.85×10^{12}, to magenta for 4.92×10^{13} NCs, to almost pure red for 1.97×10^{14} NCs, as is demonstrated by the colored photographs of the device emission shown in Fig. 1 (a). For the sample covered by 4.92×10^{13} NCs the integrated intensity of the blue and the red emission maximum is almost the same, independent of the diode bias, as shown in Fig. 1 (b). The constant ratio between the NC emission (solid line) and the InGaN emission (symbols) across the whole operation range of the diode approves the excellent color stability achieved with the colloidal NCs as nano-phosphor. It should be mentioned that operation over several days did not lead to any change of the red-blue ratio at all.

To show that efficient color conversion can also be achieved for the infrared spectral region we have prepared also devices with PbS NCs, exhibiting their first excitonic absorption peak around 925 nm [dashed line in Fig 1 (c)]. In this case the NCs were dissolved in a PMMA-CB solution, resulting in a NC volume fraction of 6.6% in the film. The emission spectrum of a sample with 9.85×10^{13} NCs deposited on the enclosure of the LED exhibits a strong peak close to a wavelength of 980 nm [solid line in Fig. 1 (c)] in addition to the InGaN peak. By choosing PbS NCs with larger sizes the emission can be shifted to even longer wavelengths up to 1.8 µm (ref. [7]) thus the whole telecommunication wavelength region can be covered by light conversion from InGaN LEDs.

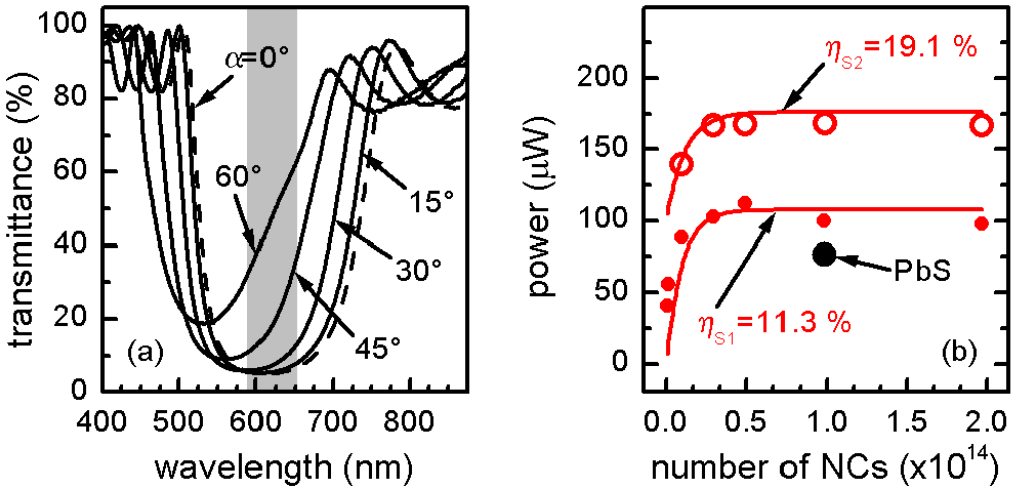

Fig. 2: (a) Transmittance spectra of the used distributed Bragg reflector for several angles of incidence. (b) Power of the color converted light from the nanocrystal quantity for sample series S1 and S2 in dependence on the nanocrystal quantity as well as for the color conversion by PbS nanocrystals.

For the series S2 we designed dielectric mirrors, which are highly reflective at the wavelength of the NC emission but transparent for the blue light from the LED. These mirrors are directly deposited onto the flat surfaces of the LED housing prior to the deposition of the NC films on top of these structures. The distributed Bragg reflectors (DBRs) consist of five pairs of TiO_2 and SiO_2 layers. For normal incidence the mirror stop-band is observed between 550 nm and 700 nm [dashed line in Fig. 2 (a)] and the stop-band center is located at a wavelength of 615 nm, matching perfectly the NC emission band, indicated as grey bar in Fig 2 (a). Outside the stop-band Fabry-Perot interference fringes appear due to multiple reflections at the mirror/air and the mirror/substrate interfaces. At 470 nm, at the emission wavelength of the InGaN LED, the transmittance is T_{470nm} = 90%. The application of such color selective mirrors markedly improves the overall performance of the devices for color conversion, by redirecting the backward directed part of the emission from the NC layer placed on top of the LED housing into the half-space in front of the device. This redirection of the color converted photons is in particular improving their extraction efficiency. The effect is already seen in the emission spectra in Fig. 1 (a) where the dashed lines, representing the measurements performed with devices coated by the color selective DBR mirrors (series S2), exhibit clearly higher intensities within the NC emission band than the uncoated devices. Due to the reflection of the mirror at 470 nm, 10% less of the LED light is absorbed by the NCs as without mirror, but almost twice as much of the NC emission is extracted from the device due to the high reflectivity band of the mirror. This is shown in detail in Fig. 2 (b) where the output power of the devices is shown as function of the amount of deposited nanocrystals. For sample series S1 the device extraction efficiency is 11.3 % whereas the application of the Bragg mirror almost doubles this efficiency to 19.1%. It is also worth to note that in the infrared, by the use of PbS nanocrystals almost the same extraction efficiency is obtained as in the visible, as shown in Fig 2 (b).

Conclusion

As an alternative to rare earth based phosphors colloidal CdSe/ZnS nanocrystals are demonstrated for light conversion from emission of InGaN LEDs to the red. For this purpose, nanocrystal films are deposited onto the enclosures of LEDs, which allows the tuning of the color of the device overall emission between blue and red, with excellent brightness dependent color stability. Color selective mirrors are applied to improve the extraction of the converted light, resulting in an almost doubling of the NC device efficiency, which is demonstrated to be almost as high for PbS NCs as for CdSe/ZnS ones.

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