Strong nonradiative energy transfer from the nanopillars of quantum wells to quantum dots: Efficient excitonic color conversion for light emitting diodes

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Abstract: Efficient nonradiative energy transfer is observed from nanopillars of InGaN/GaN quantum wells to colloidal CdSe/ZnS quantum dots up to 83% efficiency. Nanostructured architecture is shown to promote excitonic color conversion for LED applications.

OCIS codes: (260.2160) Energy transfer; (160.4236) Nanomaterials; (230.5590) Quantum-well, -wire and -dot devices

Luminescent semiconductor nanocrystal quantum dots (NQDs) are among the strongest candidates as prospective color converting systems to substitute for phosphors in white light-emitting diodes (LEDs). Among the favorable optical properties of NQDs are their comparatively narrow emission widths, enabling color purity, and precise tunability of color, allowing for color quality when used in right combinations. In the state-of-the-art LED technology, which most commonly relies on the method of color conversion to generate the white light spectrum, high photon energy pump LEDs (e.g., an InGaN/GaN based blue-emitting LED chip) excite the color converting coatings to perform photon down-conversion. [1] Typically, this conversion is solely based on radiative energy transfer. As a complementary technique, Förster-type nonradiative energy transfer (NRET) based on dipole-dipole coupling introduces an additional channel in the conversion process. [2] To date various NRET enhanced color converters have been reported. However, these include only planar epitaxial layer architectures [2] and those with elliptical cross-sectioned holes [3]. Different than these previous reports, in this work, we propose and demonstrate a hybrid system consisting of the nanopillars of epitaxial InGaN/GaN multiple quantum wells (MQWs) integrated with colloidal CdSe/ZnS core/shell NQDs. This nanopillar architecture enables strong NRET from MQWs to NQDs, which is intended to allow for efficient excitonic color conversion LEDs. [4] The resulting enhancement in NRET is attributed to the increased interaction volume between the donor MQWs and the acceptor NQDs in the hybrid architecture (Figure 1).

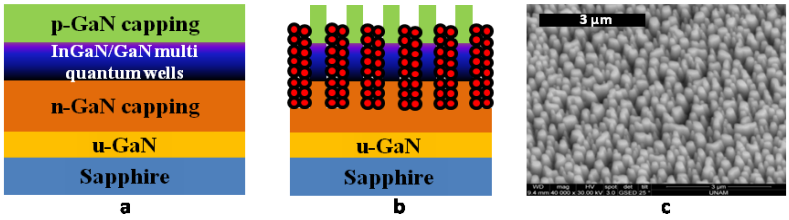

Fig.1. Schematics of (a) the planar LED epitaxy and (b) the nanopillar architecture furnished with NQDs, and (c) scanning electron microscopy (SEM) image of the nanopillars (the scale bar is 3 µm).

Epitaxial wafers consisting of InGaN/GaN MQWs are grown with metal organic chemical vapor deposition (MOCVD) (Figure 1(a)). The array of nanopillars is fabricated using nanopatterning, and CdSe/ZnS NQDs (emitting in green, orange and red) are subsequently integrated within the nanopillars (Figure 1(b)). For nanopatterning, Ni clusters are formed as a hard mask on the epi-wafer to define the nanopillars with inductively coupled plasma reactive ion etching (Figure 1(c)). This nanostructured architecture exhibits increased photoluminescence intensity as compared to its planar counterpart, which results from increased strain relaxation and extraction efficiency. Also, a strong spectral overlap exists between the emission of these MQW nanopillars and the absorption of the integrated NQDs, which is required for efficient NRET. In this hybrid architecture, NRET dynamics is studied through time-resolved fluorescence spectroscopy. As an exemplary case, Figure 2(a) shows transient photoluminescence decays of the donor MQWs in the absence and presence of the green, orange and red emitting NQDs. When the NQDs are introduced, the transient photoluminescence of the MQWs decays faster. This indicates that a new de-excitation channel for the MQWs has been unlocked, which competes for the depletion of the excited states in the MQWs. In

Figure 2(b) the steady state photoluminescence of the MQWs before and after the integration of these green, orange and red NQDs is depicted. Almost a complete color conversion is achieved as a result of efficient NRET, as seen in Figure 2(b).

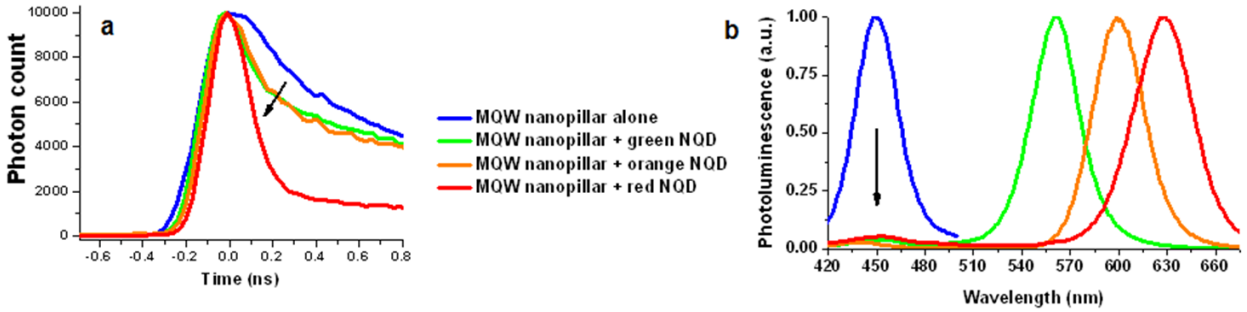

Fig.2. (a) Time resolved photoluminescence at the MQW emission wavelength and (b) steady state photoluminescence of the MQWs with and without incorporation of the green, orange and red emitting NQDs.

The NRET dynamics including the rates and efficiencies are further analyzed using the results of the time resolved fluorescence spectroscopy. The highest measured energy transfer efficiency level of 83% with an energy transfer rate of $(0.192\ \text{ns})^{-1}$ is observed with the utilization of red emitting NQDs at room temperature. This energy transfer efficiency is found to be a record for the hybrid systems of epitaxially grown MQWs with NQDs. This results from the nanopillar architecture, which allows for the intimate integration of NQDs. By changing the NQD size, which also changes the effective band gap, the energy transfer rates are tuned to $(0.237\ \text{ns})^{-1}$ and $(0.253\ \text{ns})^{-1}$ for the orange and green emitting NQDs, respectively. NRET efficiencies are still around 80% for these NQDs.

Furthermore we model the NRET channel based on Förster-type dipole-dipole coupling between the MQWs and the NQDs. The energy transfer rate is driven for a two-dimensional quantum well donor and a sheet of zero dimensional quantum dot acceptor, which is given by

$$k_{ET} = \frac{k_D 0.5\pi\sigma {R_o}^6}{d^4} \quad (1)$$

where k_D is the de-excitation rate of the donor MQW excited state in the absence of NQD acceptors, σ is the NQD density, R_o is the Förster radius, d is the actual separation between the NQDs and the MQWs. Unlike typical Förster resonance energy transfer between molecules, here the transfer rate scales with d^{-4} as a result of the geometry. Also, it is worth pointing out that Dexter-type energy transfer is not possible in our hybrid system because TOPO ligands (~1.1 nm) and ZnS shell (~0.6 nm) of the CdSe/ZnS NQDs strongly confine the electron wave-function inside the CdSe core, so that direct charge transfer is unlikely. Theoretical results for the NRET dynamics are calculated using k_D values from the experiments, d and σ from the material properties of the NQDs, and Förster radius, R_o, from the spectral overlap function. Theoretically the calculated energy transfer rates are $(0.197\ \text{ns})^{-1}$, $(0.230\ \text{ns})^{-1}$, and $(0.248\ \text{ns})^{-1}$ for the integrated red, orange and green emitting NQDs, respectively. These are in very good agreement with the experimentally measured energy transfer rates of $(0.192\ \text{ns})^{-1}$, $(0.237\ \text{ns})^{-1}$, $(0.253\ \text{ns})^{-1}$ supporting that the energy transfer between the MQWs and the NQDs is mainly due to long-range Förster-like dipole-dipole coupling.

In conclusion, we presented efficient exciton injection from InGaN/GaN multiple quantum well nanopillars to CdSe/ZnS core/shell nanocrystal quantum dots through Förster-type nonradiative energy transfer. Increased interaction volume between the MQWs and the NQDs in this nanostructured hybrid architecture led to a strong NRET, which is intended to complement the radiative energy transfer to increase the overall efficiency of the color conversion LEDs. By varying the effective band gap of core/shell NQDs, the excitonic energy transfer rates for these NQD integrated hybrids were conveniently controlled and tuned. A record NRET efficiency of 83% was achieved with the integration of red emitting NQDs with blue emitting MQW nanopillars. The measured and computed exciton transfer rates were found to be in excellent agreement for all hybrid cases.

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