Project **Ref. nr 11-161 “Development of hybrid light emitting diode structures”**

Final report 2014-12-31

Summary

III-nitride-based hybrid heterostructures for light emitting diodes (LED) combine advantages of epitaxially grown semiconductor quantum wells (QW) with inexpensive polymers or colloidal nanoparticles having efficient fluorescence in the visible region. Such hybrid LED are promising for fabrication of low-cost and highly efficient microlight sources that can be used in full-color displays, imaging systems, miniature chemical and biological sensors. The light is down converted in the typical organic/inorganic GaN-based LED hybrids from UV emission to visible via common radiative energy transfer. The aim of the project was to develop a novel class of hybrid structures utilizing a non-radiative (Förster) resonant energy transfer (NRET) from excitation generated in inorganic QWs to excitons in organic films. According to theoretical predictions such hybrids might be considerably more efficient compared to their radiative analogues. Within the project several hybrid structures have been fabricated and studied. Both green polyfluorene and colloidal ZnO nanocrystals have been used for deposition as a fluorescent film on the top of AlGaN/GaN QW structures. The top layer AlGaN thickness has to be less than 4 nm to allow a dipole-dipole interaction and, thus, an efficient pumping energy transfer even at room temperatures.

Tasks planned for the project:

The following tasks were planned to be studied:

1. To study hybrids based on the organic/inorganic AlGaN/GaN QW structures utilizing non-radiative energy transfer with different cap layer thickness.

2. To fabricate hybrid structures using colloidal materials as a fluorescent film.

3. To evaluate the non-radiative energy transfer efficiency for different fluorescent films.

4. To study the operation time/degradation of hybrid structures fabricated with colloidal nanocrystals film.

5. To study of the quality of the interface region between semiconductor QW and organic/colloidal film and its influence on NRET

Results achieved within the project 2011-2014.

We have followed the planned activity and found answers for the main tasks. Results related to the project were presented at several international conferences and are published in high-impact international scientific journals.

We have fabricated and studied hybrid structures based on AlGaN/GaN QW and green polyfluorene. We have found effect of non-resonant energy transfer (NRET) for structures with thin (4 nm) space layer between semiconductor and polymer material. We have also found that exciton localization influences the energy transfer efficiency in such organic/inorganic QW hybrid structures. The effect could be seen experimentally as a strong increase of the energy transfer rate with temperature in the interval of 5-100 K (see Fig.1). The NRET efficiency at room temperature was found to be 22 % which exceeded room temperature by orders a room temperature efficiency obtained for radiative energy transfer hybrid LED structure (0.15 %).

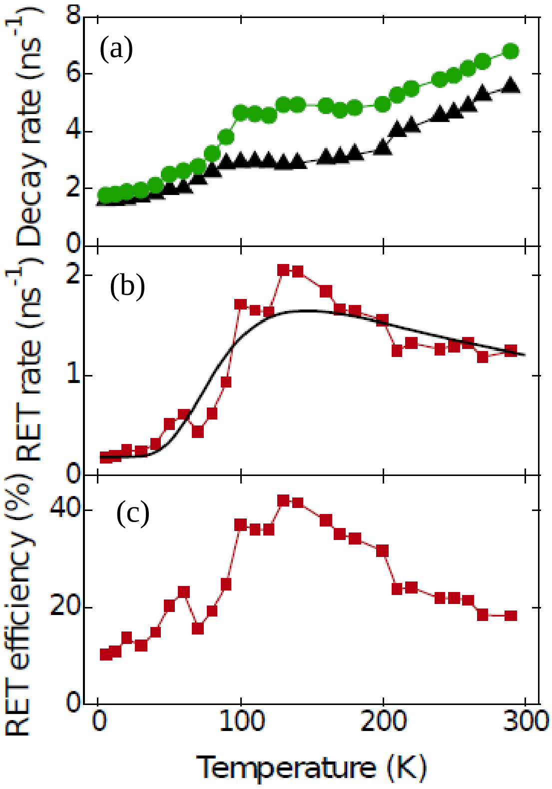

Fig. 1 (a) PL decay rate of the QW exciton before (black) and after (green) deposition of the polyfluorene at 100 K. (b), (c) Energy transfer rate and efficiency at different temperatures.

The ZnO nanocrystals (NCs) have been investigated as a potential material for new ZnO/GaN QW hybrid structures. ZnO NCs satisfies the requirement of absorption overlapping with GaN emission (a room temperature band gap energy is 3.3 and 3.4 eV for ZnO and GaN, respectively), which is presented in Fig.2.

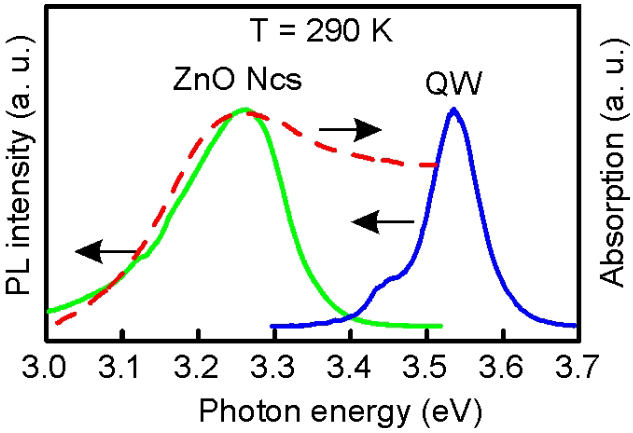

Fig.2. Room temperature PL and absorption spectrum for ZnO NCs together with the AlGaN/GaN QW emission shows a good overlap between absorption of energy acceptor material (i.e. ZnO) and energy donor material (i.e. AlGaN/GaN QW).

Different type of ZnO nanocrystals (NCs) were used for fabrication of hybrid QW structures. We have synthesized ZnO NCs by sol-gel method as well as we have used ZnO NCs suspended in butyl acetate, ethanol, and water. Some of ZnO NCs were supplied by the company SIGMA-ALDRICH. To avoid ZnO NCs from aggregation into bigger clusters, the mixture of ZnO NCs and solvent was put in the ultrasonic bath and after that deposited by spin-coating on the GaN/AlGaN QW samples with three different thicknesses of the cap layer. Morphology and quality of the ZnO NCs films has been studied by scanning electron microscopy (SEM) and by transmission electron microscopy (TEM). Example of TEM image together with a schematic of the hybrid structure is illustrated in Fig. 3.

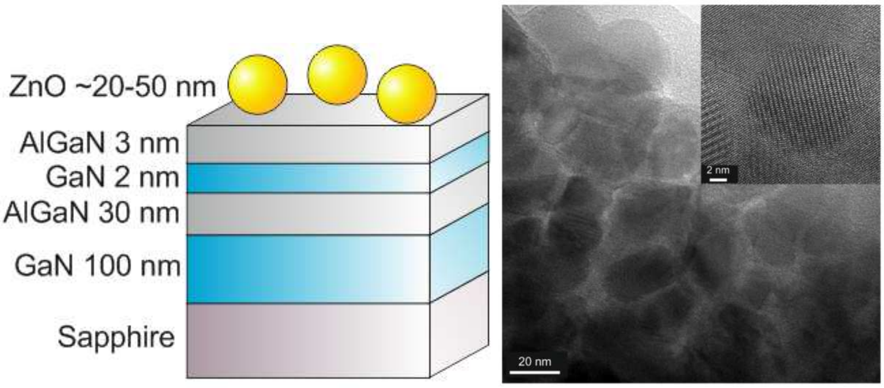

Fig. 3. Schematic drawing of hybrid ZnO/AlGaN/GaN structure. TEM image showing size of ZnO nanocrystals, while crystalline quality with lattice fringes corresponding to wurtzite structure is depictured in the inset.

To investigate NRET efficiency, the time-resolve photoluminescence (TRPL) has been studied for hybrids fabricated with ZnO nanocrystals and for pure QW structures. The rate of energy transfer can be estimated from the comparison of the QW exciton recombination time with and without acceptor material, i.e. ZnO NCs. For the bare QW structures the recombination rate k_{QW} has contribution of radiative and non-radiative recombination components: $k_{QW} = k_r + k_{nr}$. For the hybrid structures assuming only one additional non-radiative recombination mechanism (i.e. NRET) it can be written: $k_H = k_r + k_{nr} + k_{ET}$ and, thus, NRET can be determined from the measured exciton recombination rates in the hybrid and in the bare QW as $k_{ET} = k_H - k_{QW}$.

Transient properties of QW excitons in the hybrids and in the bare QW samples have been analyzed in dependence on the QWs cap layer thickness. We have observed a clear effect related to NRET even at room temperature for samples with the thinnest cap layer (3 nm). We have found a best NRET efficiency at 60 K as shown reaching ~45 % (Fig.4), while no NRET effect can be observed in hybrids fabricated using control samples with thicker spacer layers. These values of NRET efficiency is ~2 orders of magnitude higher than for common radiative energy transfer hybrid LEDs.

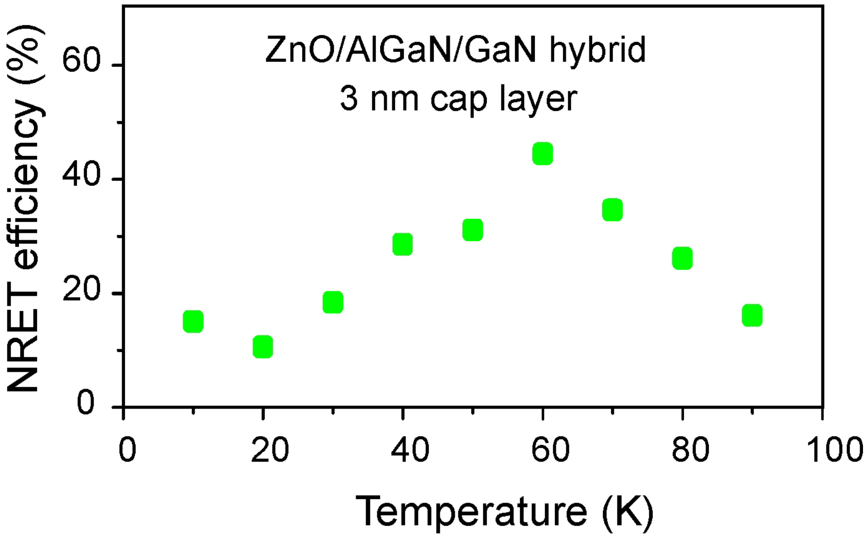

Fig.4. NRET efficiency as a function of temperature for the structure with the AlGaN barrier thickness of 3 nm.

A stability of NRET in hybrid structures was studied under some thermal treatment (such as cooling-heating). Despite that ZnO nanocrystals are stable and do not show any degradation of their properties, we have observed the degradation of hybrids fabricated using ZnO nanocrystal coatings. Such degradation, which can be caused by degradation of the interface quality due to thermal treatment such as cooling or as a result of ambient influence such as humidity, leads to decreasing of NRET efficiency after some time (after several months).

We have observed a complicated behavior of the QW excitons in the studied hybrids related to the changing of the surface potential. We have found that the QW exciton lifetime decreases for hybrids compared to the bare QW structures with the thinnest (3 nm) cap layer, while the QW PL decay became slower up to 200 K in the coated structure with the spacer thickness of 6 nm. No difference in the thermal behavior of the QW exciton lifetime was found between coated and uncoated structure with a 9 nm-thick cap layer. An increase of surface potential barrier is suggested as an additional mechanism, besides NRET, affecting QW exciton lifetime in hybrids. The later observation shows the importance of interface properties for fabrication of hybrid structures. Fig. 5 shows that there is no noticeable influence of the ZnO NCs film on the exciton dynamic in the sample with 9 nm cap layer, while there is a clear effect of the coating on the exciton temporal behavior in hybrids with thinner spacer. However, the tendency is opposite in two cases, i.e. for samples with 3 and 6 nm cap layer thickness.

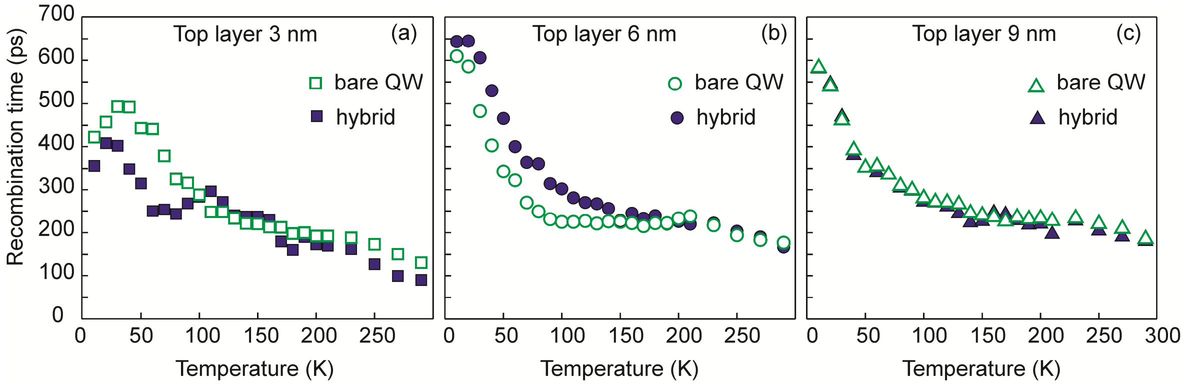

Fig.5. Extracted recombination time of the QW exciton shown as a function of temperature for the hybrids (solid signes) and for the uncoated samples (open signes) with the top layer thickness of (a) 3 nm, (b) 6 nm, and (c) 9 nm.

Thus, we suggest that there are several possible factors having opposite impact on the QW exciton recombination. We have done calculation of the influence of the surface potential on electron states in samples with 3, 6 and 9 nm cap layer thicknesses and have shown, that the possible change of the surface potential in hybrids has to be taken into account when the NRET efficiency is extracted from TRPL measurements. The results are accepted for publications in Scientific Reports, Nature Publishing Group (2014).

Publications related to the project

The dependence of resonance energy transfer on exciton dimensionality. J.J. Rindermann, G. Pozina, B. Monemar, L. Hultman, Hiroshi Amano, and P. G. Lagoudakis, Phys. Rev. Lett. 107, 236805 (2011).

The effect of exciton dimensionality on resonance energy transfer: advances for organic color converters in hybrid inorganic/organic LEDs. Jan Junis Rindermann, Galia Pozina, Bo Monemar, Lars Hultman, Hiroshi Amano, and Pavlos G. Lagoudakis, Proc. SPIE 8255, 82550I (2012).

Surface potential effect on excitons in AlGaN/GaN quantum well structures. G. Pozina, C. Hemmingsson, H. Amano, and B. Monemar, Appl. Phys. Lett. 102, 082110 (2013)

Dynamic properties of excitons in ZnO/AlGaN/GaN hybrid nanostructures. Mathias Forsberg, Carl Hemmingsson, Hiroshi Amano, and Galia Pozina, Sci. Reports; Nature Publishing Group, 2014 (accepted).

The following topics related to the project were presented at the international conferences:

1. SPIE Photonics West 2012, 21.-26 January 2012, San Francisco, USA

Presentation: The effect of exciton dimensionality on resonance energy transfer: advances for organic color converters in hybrid inorganic/organic LEDs. J. J. Rindermann, G. Pozina, B. Monemar, L. Hultman, H. Amano, P. G. Lagoudakis

2. The 31st international conference on the physics of semiconductors. July 29th to August 3rd 2012, Zurich, Switzerland

Presentation: Towards efficient organic/inorganic hybrid LEDs: the Effect of Exciton Dimensionality on Resonance Energy Transfer. Jan Junis Rindermann, Galia Pozina, Bo Monemar, Lars Hultman, Hiroshi Amano, and Pavlos G. Lagoudakis

3. XI International Conference on Nanostructured Materials. 26-31 August, 2012, Rhodes, Greece

Presentations: Studies of hybrid structures based on ZnO nanocrystal and AlGaN/GaN quantum wells. G. Pozina, C.Y. Kuo, M. Forsberg, H. Amano, and L. Hultman

4. International Workshop on the Physics of Excitons 2013. March 30 - April 22, 2013, Varadero, Cuba

Presentation: Near surface potential effect on excitons in AlGaN/GaN quantum wells. G. Pozina, C. Hemmingsson, H. Amano, and B. Monemar

5. E-MRS 2013 Spring Meeting, 27-31 May, 2013, Strasbourg, France

Presentation: Investigation of Hybrid Structures based on III-Nitrides. M. Forsberg, Ching-Lien Hsiao, H. Amano, L. Hultman, and G. Pozina.

6. International Conference on Metamaterials and Nanophysics, 22 April- 1 May, 2014, Varadero, Cuba.

Invited talk: HVPE growth of GaN: from nanostructures to bulk substrates. Galia Pozina and Carl Hemmingsson

7. AFM2014 - Advanced Functional Materials Conference, 20 - 21 August 2014, Kolmården Vildmarkshotell, Norrköping, Sweden.

Presentation: III-N quantum well structures for non-radiative energy transfer studies. Mathias Forsberg, Ching-Lien Hsiao and Galia Pozina

8. CeNano Symposium, 27 November 2014, Linköping, Sweden.

Presentation: Organic/inorganic hybrid structures fabricated utilizing III-N nanorods, Mathias Forsberg, Alexandra Serban, Ching-Lien Hsiao and Galia Pozina.