Plasmon-enhanced Energy Transfer in a Hybrid System using Silver Nanobox Array Geometries

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***Abstract* – Silver metal nanobox arrays are used to demonstrate plasmon-enhanced non-radiative energy transfer from an InGaN/GaN quantum well to a ~80 nm thick layer of CdSe/ZnS quantum dots embedded in PMMA. Three arrays of varying periodicity are fabricated by helium-ion lithography. Plasmon-enhanced non-radiative energy transfer efficiencies up to 30% are observed from the quantum well to the quantum dots, despite no signatures of non-radiative energy transfer being detected in the absence of the silver nanobox arrays. It is shown that by tuning the Ag nanobox array periodicity the acceptor QD emission can be optimized to benefit from both non-radiative energy transfer and direct plasmonic enhancement of the QD emission.**

I. INTRODUCTION

In this work, we investigate three different silver nanobox arrays for localised surface plasmon - enhanced non-radiative energy transfer (LSP-NRET) in a hybrid quantum well (QW) – quantum dot (QD) structure. The Ag nanobox arrays are fabricated using helium-ion lithography (HIL) on top of a 3 nm thick capping layer of a single donor InGaN/GaN QW. The acceptor CdSe/ZnS QDs are embedded in a ~80 nm thick PMMA layer. Non-radiative energy transfer from QWs to QDs has already been demonstrated for colour-conversion or white light LEDs. Due to the limited energy transfer range, the structures required single QDs monolayers or etched holes filled with QDs. Plasmonic enhancement of the energy transfer range and efficiency would allow for less complex designs and an increased number of possible acceptors. HIL allows for very accurate fabrication of highly ordered and periodic structures on the nanoscale. This level of control over the size, shape and periodicity of the nanostructures enables sensitive tailoring of the surface plasmon resonance (SPR) and the local electromagnetic field. In this study the shape and size of the individual nanoboxes are fixed but the periodicity within the array is varied. The nanobox array can separately influence the QW and QD emission as well as the LSP-NRET between them. LSP –coupled emission and LSP-NRET are sensitive to SPR properties, such as the spectral overlap with emission and/or absorption features and the local field strength [1-2]. We use time-resolved photoluminescence (TRPL) and PL spectral measurements to investigate the impact of the silver nanoboxes on both the LSP-NRET and the total emission from the three-component system.

II. RESULTS AND DISCUSSION

A schematic of the is shown in Fig. 1(a). The TRPL decay curves are fit with a bi-exponential and the average PL lifetime is given by Eqn.1,

$$\tau_{avg} = \frac{I_1 * \tau_1^2 + I_2 * \tau_2^2}{I_1 * \tau_1 + I_2 * \tau_2} \ , \qquad (1)$$

where I_1 and I_2 are the intensity amplitudes for the exponential decays with two different lifetimes τ_1 and τ_2, respectively.
hree different nanobox arrays are investigated in this work, labelled Box 1, Box 2 and Box 3. They consist of silver nanoboxes with a lateral dimension of 100nm, height of 35 nm and separations of 100nm, 130nm and 160nm, respectively. A S.E.M. image of the Box 1 array is shown in Fig. 1(b). It can be seen that the large array of boxes is very uniform and that the aspect ratio of the individual boxes is well maintained. Fig. 1(c) shows the emission spectra of the QW and the QDs, the absorption spectrum of the QDs and the extinction spectra for the three nanobox arrays.

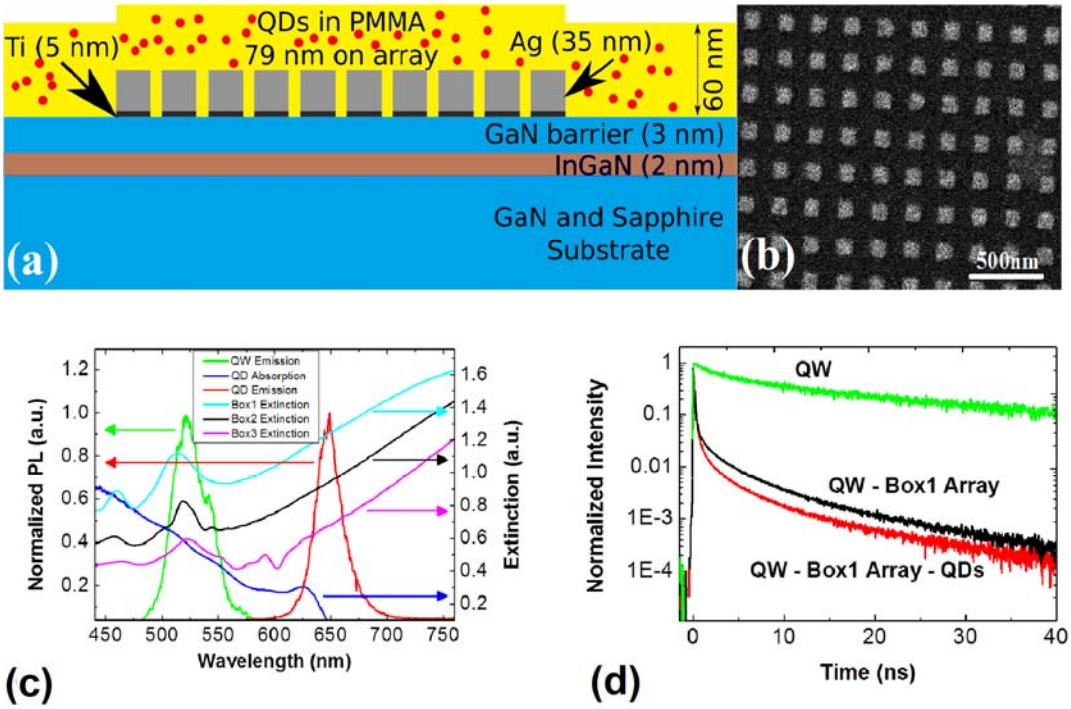

Fig.1. (a) Schematic of full hybrid structure. (b) S.E.M. image of NanoBox 1 structure. (c) The normalized emission spectra of the QW and QDs along with the absorption spectrum of the QDs and the theoretically modeled extinction spectra of the three Ag nanobox arrays. (d) Normalized PL decay curves of QW by itself (green line), QW on the Box1 array (black line) and QW on Box1 array after deposition of the QD layer (red line).

The QW TRPL decay curves for the QW only, the QW with Box1 array fabricated on top of the capping layer and for the full structure with the QD layer, is shown in Fig. 1(d). The QW and QW-nanobox array structures are also coated with a ~80 nm thick PMMA layer to allow for direct comparison. The reduction of the QW lifetime and PL emission when measured on the Box1 array is a signature of quenching of the QW emission by the nanobox array. The quenching efficiency is quantified by Eqn.2. [3].

$$E_Q = 1 - \frac{\tau_{QW-NB}}{\tau_{QW}} \tag{2}$$

The further reduction in the QW lifetime after the deposition of the QDs is a signature of LSP-NRET from the QW to the QDs. The LSP-NRET efficiency is given by Eqn.3 [3].

$$E_{NRET} = 1 - \frac{\tau_{QW-NB-QD}}{\tau_{QW-NB}} \tag{3}$$

Using both Eqn.2 and Eqn.3, the quenching and LSP-NRET efficiencies are calculated for all three nanobox structures, shown in Fig. 2(a). For all three nanobox arrays it can be seen that the quenching efficiencies are approximately 90% and that the plasmon-enhanced energy transfer efficiencies vary from ~25% - 30%. Therefore, the three nanobox structures appear to facilitate similar levels of NRET from the QW to the QDs. It can be noted that there is no evidence of NRET from the QW to the QD layer in the absence of the nanobox arrays.

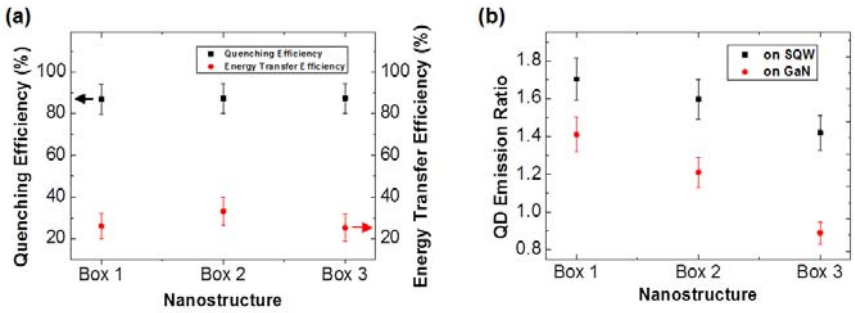

Fig. 2. (a) Quenching efficiencies and plasmon-enhanced energy transfer efficiencies as a function of nanobox structure. (b) QD emission ratio on both QW and bulk GaN substrates as a function of nanobox structure.

Now we consider the impact of the change in nanobox array periodicity on the total emission from the hybrid system. Strong quenching of the QW emission has been noted above. To investigate the impact of the different nanobox arrays on the QDs, the QD emission ratio (QD emission on the structure/QD emission off the structure) on both the SQW and bulk GaN substrates for all three nanobox structures is plotted in Fig. 2(b). The QD emission ratio on the GaN substrate shows the effect of any enhanced absorption or emission of the QDs due to the presence of the nanobox arrays alone. The QD emission is quenched on Box3 and enhanced on Box1 and Box2 structures, respectively. Subsequently, by examining the QD emission on the SQW substrate with and without the nanobox arrays we can isolate the contribution of the LSP-NRET process. It can be seen that the QD emission is now further enhanced for all three structures on the SQW. The LSP-NRET has facilitated a significant increase in the QD emission for all structures. Additionally, by tuning the array periodicity it is possible to optimize the QD emission benefitting from both LSP-NRET and direct enhancement of the QD emission, The QD emission enhancement varies from 43% for Box3 to 71% for Box1.

III. CONCLUSION

In conclusion, we have demonstrated LSP-NRET from an InGaN/GaN QW to a layer of QDs embedded in PMMA using Ag nanobox arrays fabricated by HIL. Three nanobox array geometries with different periodicities were fabricated to investigate their impact on the LSP-NRET and overall QD emission. In the absence of the nanobox arrays there is no measureable direct NRET from the QW to the QD layer. It is found that nanoboxes substantially increase the LSP-NRET efficiency to ~30% despite strong direct quenching of the QW emission. The LSP-NRET did not show strong sensitivity to the periodicity. However, the QD emission enhancement could be optimized by tuning the periodicity. The emission enhancement had contributions from both direct LSP-enhanced emission and LSP-NRET. QD emission enhancements of up to 71% were observed.

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