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Coupling of InAs/InP quantum dots to the plasmon resonance of In nanoparticles grown by metal-organic vapor phase epitaxy

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We report strongly modified optical emission of InAs/InP quantum dots (QDs) coupled to the surface plasmon resonance (SPR) of In nanoparticles grown by metal-organic vapor phase epitaxy. With increasing In deposition time, the In nanoparticle size increases and the SPR redshifts significantly. When overlapping with the SPR, the excited state photoluminescence of the QDs is strongly enhanced due to QD-SPR coupling while the ground state photoluminescence is quenched due to non-radiative energy transfer. This is underpinned by the wavelength dependence of the spontaneous emission decay time which shows an opposite trend compared to that of bare QDs. © 2013 AIP Publishing LLC.

Semiconductor quantum dots (QDs) possess unique characteristics for next-generation photonic devices due to the three-dimensional quantum confinement of carriers. Of particular interest is the enhancement of the optical properties of the QDs through modification of the local optical density of states (DOS) in the surrounding medium. For instance, when locating the QDs close to a metal surface or to surface plasmons have been observed, which offer an efficient means to tailor the interaction between QDs and the electromagnetic field. Recent works have demonstrated surface plasmon enhanced emission of a coupled system of InAs/GaAs QDs and In/Ag metallic nanoparticles which have been spatially aligned by strain correlated epitaxial growth.1–3 One of the interesting properties we have observed is that the photoluminescence (PL) from the QDs is modified so strongly due to direct QD exciton-surface plasmon coupling that an additional emission peak corresponding to the surface plasmon resonance (SPR) appears. This phenomenon provides the possibility to tailor the optical properties of the QDs and to enhance the emission at desired wavelengths by tuning of the SPR supported by the metallic nanostructures. All this requires single nanometer precise control of the distance between the metallic nanostructures and the QDs to balance non-radiative energy transfer from the QDs to the metallic nanostructures for too short distance6 and the strongly decaying evanescent surface plasmon field. A distance around a few nanometers is optimum to achieve plasmonic enhancement of the QD emission.3 Full insight into the different mechanisms can only be provided by investigating the time-dependent optical response of the QDs coupled to metallic nanostructures in addition to the static emission properties.

In this work, we study the coupling of InAs/InP QDs to the SPR of In nanoparticles that are grown by metal-organic vapor phase epitaxy (MOVPE). With increasing size of the In nanoparticles, the SPR redshifts significantly. When overlapping, the SPR strongly enhances the emission due to excited state (ES) transitions of the QDs around 1310 nm, while the emission due to QD ground state (GS) transitions is quenched due to non-radiative energy transfer. This is confirmed by time-resolved PL (TRPL) showing a pronounced decrease of the spontaneous emission decay time as a function of wavelength in the two wavelength regimes. This behavior is opposite to the trend observed for bare QDs where the spontaneous emission decay time monotonously increases with wavelength.

The samples were grown by MOVPE on (100)-oriented InP substrates with 2° misorientation towards the (110) facet. Tertiarybutyl-arsine (TBA), tertiarybutyl-phosphine (TBP), trimethyl-gallium (TMG), and trimethyl-indium (TMI) were used as precursors with H2 as carrier gas. The V/III flow ratios for GaAs and InAs growth were 1:17 and 0.62, respectively. The growth of the sample structure commenced with a 100 nm thick InP buffer layer at the temperature of 517 °C. This was followed by a 1.3 monolayer (ML) GaAs interlayer, a single layer of 2 ML InAs QDs, 10 s growth interruption under TBA flow, and an InP cap layer with different thickness, all at the same temperature. Then the samples were cooled down to 350 °C and the In nanoparticles were grown by exposure to TMI flux for time durations of 1 to 25 min.8 Control samples with In nanoparticles directly deposited on InP and InAs QDs without In nanocrystals on top have been also prepared in order to independently investigate the SPR wavelengths of the In nanoparticles and the optical emission from the InAs QDs.

First, the control samples with In nanoparticles deposited directly on InP are characterized. Figure 1(a) shows the SPR of the In nanoparticles measured by differential reflectivity (DR) spectroscopy at room temperature (RT).9 The SPR peaks are centered at 619, 759, 950, and 1380 nm for In deposition times of 1, 3, 10, and 25 min, respectively. A strong redshift of the SPR peaks is observed with increasing...
In deposition time. The kink occurring in the DR spectra at 920 nm is due to the abrupt refractive index change which is caused by the band edge absorption of bulk InP. The redshift of the SPR resonances is in accordance with the increase of In nanoparticles size with In deposition time, which is consistent with previous reports on metallic nanoparticles. This is documented in Fig. 1(b) where the average height of the In nanoparticles determined from atomic force microscope (AFM) measurements is plotted versus the corresponding SPR wavelength. In the following experiments, we concentrate on the In nanoparticles formed for 25 min deposition time exhibiting the SPR in the important 1.3 μm telecom wavelength band (O-band).

Figures 2(a) and 2(b) present the AFM images of the surface morphology of the uncapped InAs QD layer and the In nanoparticles for 25 min In deposition time on the InAs QDs capped with 6 nm InP, respectively. The QDs exhibit an average height of 5.5 nm with QD density of $2.5 \times 10^{10}$ cm$^{-2}$. The In nanoparticles have an average height of 74 nm with density of $2.5 \times 10^9$ cm$^{-2}$. On average, one In nanoparticle covers about 10 QDs. The In nanoparticles have a largely dispersed size distribution, in particular regarding the diameter, which explains the very broad DR spectra.

The coupling between the In nanoparticles and QDs is initially studied by PL spectroscopy for different InP cap layer thicknesses and with the PL from bare InAs QDs as reference. The red curve in Fig. 3 shows the PL spectrum of the QD-metal hybrid structure with 6 nm InP cap layer, the blue curve shows the PL spectrum for 20 nm cap layer, and the black curve shows the PL spectrum of the bare InP QDs capped with 6 nm InP, all measured at 7 K. The PL spectrum of the bare QDs exhibits an emission peak beyond 1470 nm which is the cut-off of the InGaAs detector. This emission is due to the QD ground state transitions. Hence, we conclude that with weaker intensity. Hence, there is no QD-SPR coupling, as the cap layer is too thick, and the In nanoparticles simply shadow off the QD emission. Only the PL spectrum of the QD-metal hybrid structure with 6 nm cap layer is significantly different. The PL exhibits a peak centered at 1310 nm with full width at half-maximum of 180 nm and a shoulder at the long wavelength side starting around 1400 nm. The peak centered at 1310 nm closely matches with the peak of the SPR of the In nanoparticles and the shoulder at the long wavelength side coincides with the onset of the emission due to the QD ground state transitions. Hence, we conclude that the peak at 1310 nm is due to plasmon enhanced emission from excited state transitions of the QDs, while the emission due to the QD ground state transitions is quenched. No significant polarization dependence of the QD emission is observed, which is in good agreement with the AFM data showing no anisotropy of the In nanoparticle shapes, resulting from the strain insensitive growth mode of the liquid In droplets, which differs from our previous reports on the strain engineered alignment of metallic nanoparticles.

To further study the coupling mechanism, TRPL measurements are carried out by exciting the QDs with a semiconductor pulsed diode laser emitting at 750 nm. The pulse duration is around 100 ps and the excitation energy is $0.2 \mu J/cm^2$ per pulse. The signal is selected spectrally by 12 nm bandpass filters with center wavelengths varying from 1200 to 1600 nm. After filtering, the signal is resolved temporally using time-correlated single photon counting with a superconducting single photon detector working at liquid Helium temperature below 2.0 K. Figure 4(a) presents the spontaneous emission decay curves measured at different wavelengths. By fitting the initial part of the decay curve with a single exponential function, the wavelength dependence of the spontaneous emission decay time is obtained, which is presented in Fig. 4(b) (red solid curve with filled circles). Both the PL spectrum (red dashed curve) and the DR spectrum (black dashed curve) are overlaid for comparison. In the wavelength region of enhanced emission from the excited states of the QDs, indicated by the grey shaded area, which matches with the maximum of the SPR, the spontaneous emission decay time decreases. This is the clear indication for plasmon enhanced emission. For longer
wavelengths, the decay time does not increase, as expected when leaving the plasmon resonance but shows a short plateau and then further decreases in the wavelength range of the QD ground state emission. This reveals that the emission due to the QD ground state transitions is quenched not only because of the enhancement of the excited states emission but that additionally non-radiative recombination plays a role. It should be stressed here that the wavelength dependence of the spontaneous emission decay time of the QD-metal hybrid structure is qualitatively different compared to that of the bare InAs QDs capped with 6 nm InP, shown in Fig. 4(c). The spontaneous emission decay time increases with increasing wavelength, which reproduces the very similar behavior as reported previously for InAs/GaAs QDs due to the increasing carrier confinement in larger, longer-wavelength QDs. This confirms the strong modification of the optical emission of the QD-metal hybrid structure due to both surface plasmon effects and non-radiative channels caused by energy transfer from the QDs to the metallic nanostructures due to QD dipole-metal interactions, established in Ref. 6. In case of high radiative efficiency of the ground state transition of the bare QDs, the presence of metal nanoparticles cannot further enhance the emission, besides the ground state emission is not overlapping with the plasmon resonance. Clearly, our results state that in the present structure, the balance is favorable for strong enhancement of the excited states emission overlapping with the plasmon resonance. Qualitatively, the metal-QD system can be described by a simplified rate equation model as the following:

\[ D_e \frac{dn_e}{dt} = \alpha P \frac{D_e}{\tau_e} - D_e \frac{n_e}{\tau_{m,e}} - D_e \frac{n_e}{\tau_{rel}}, \]  

(1)

where \( n_e \) and \( n_g \) are the carrier densities at the ES and GS of QDs, respectively, \( D_e \) and \( D_g \) are the carrier density of states of the ES and GS, respectively, \( \tau_e \) and \( \tau_g \) are the carrier lifetimes of the ES and GS, respectively, \( \tau_{m,e} \) and \( \tau_{m,g} \) are the metal related nonradiative decay times at the ES and GS, respectively, \( \tau_{rel} \) is the carrier relaxation time from the ES to GS, \( P \) is the pumping rate, \( \alpha \) is the quantum efficiency of the pumping, and \( F \) is the Purcell factor. Here, we adopt a weak excitation assumption so that the carrier relaxation is not related to the state filling in the GS.

At the steady state, by setting the left hand sides of Eqs (1) and (2) to be zero, we get

\[ n_e = \frac{\alpha P}{D_e F} \frac{1}{\tau_e + \frac{1}{\tau_{m,e}} + \frac{1}{\tau_{rel}}} \]  

(3)

and

\[ n_g = \frac{\alpha P}{D_g} \left( \frac{1}{\tau_g + \frac{1}{\tau_{m,g}}} \right) \]  

(4)

In the experiment, the ES emission is larger than the GS emission, hence it requires

\[ D_e F \frac{n_e}{\tau_e} \geq D_g \frac{n_g}{\tau_g} \]  

(5)

From Eqs. (3)-(5), we obtain

\[ F \frac{1}{\tau_e} \geq \frac{1}{\tau_g + \frac{1}{\tau_{m,g}}} \]  

(6)

If there is no metal decay channel, i.e., \( \tau_m \to \infty \), Eq. (6) will not be satisfied simply because the carrier relaxation time is much shorter than the recombination time. However, if \( \tau_g \gg \tau_{m,g} \), i.e., the nonradiative decay channel dominates the GS transition, Eq. (6) can hold and the ES emission can be larger than the GS emission. The above simple model is just a brief illustration for the enhancement of the ES emission. However, this model could not fully describe the complex situation of our samples, because the nano-particles could affect the directional emission intensity since they act as a nano-antenna and the metal related nonradiative recombination rate could be even larger at the longer wavelength side (the actual GS peak is longer than 1600 nm). However, we have shown that the coupling of QDs to surface plasmons can not only enhance the emission but qualitatively alters the emission spectrum and the transitions involved.

In summary, we have studied the coupling between InAs/InP QDs and In nanoparticles grown by MOVPE. The In nanoparticle size is controlled by the In deposition time resulting in strong redshift of the SPR for larger size. When overlapping, the excited states PL emission of the QDs is

\[ D_g \frac{dn_g}{dt} = D_e \frac{n_e}{\tau_{rel}} - D_e \frac{n_g}{\tau_{m,g}} - D_g \frac{n_e}{\tau_{m,g}}, \]  

(2)
strongly enhanced due to QD-SPR coupling, while the ground state PL emission is quenched due to non-radiative decay. TRPL results underpin this behavior, showing strong modification of the wavelength dependence of the spontaneous emission decay time, confirming the coexistence of spontaneous emission enhancement due to surface plasmon effects and non-radiative recombination channels due to the closely placed metallic nanoparticles.

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