Optically Enhanced Emission of Localized Excitons in $In_xGa_{1-x}N$ Films by Coupling to Plasmons in a Gold Nanoparticle

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We report on strong site-selective enhancement of the emission of localized excitons in an $In_xGa_{1-x}N$ film, induced by resonant coupling to a single plasmon confined in a gold nanoparticle. The particle was attached to an atomic-force-microscope probe and placed at the near-field distance of the surface. The observation is explained by the enhancement of the spontaneous emission recombination rate of the excitons due to the local increase in the photonic mode density near the metal particle. The interpretation is consistent with the intensity increase and lifetime shortening of the emission observed in the same film with deposited Au clusters. We show that the nanoscale roughness of the film is an important prerequisite of the efficient plasmonic enhancement.

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Control over the emission of a single quantum emitter is an important problem of quantum science and engineering. In particular, many proposed applications in the emerging field of quantum information rely on the development of efficient solid-state single-photon sources. By now, semiconductor epitaxial quantum-dot (QD) structures have shown great potential as practical single-photon devices, because they are relatively stable, have narrow spectral linewidths, and are capable of electrical-carrier injection. The triggered single-photon sources with a QD embedded in an optical microcavity have already been demonstrated [1,2]. They exploit the so-called Purcell effect [3] that is the cavity-induced increase in the spontaneous recombination rate of the emitter. The main obstacle for commonly studied III–V quantum dots is the requirement of cryogenic temperatures. To overcome this problem, wide-band-gap nanostructures like GaN QDs [4] and CdSe QDs [5] were used to demonstrate single-photon sources up to 200 K. To increase further the operational temperature, one can insert the QD in a three-dimensional post microcavity improving the collection efficiency. However, fabrication of such a structure remains a challenge.

It is well known that the emission properties of a nanoscale optical emitter can be significantly modified by the proximity of a metal nanoparticle that supports localized plasmons (see Ref. [6] and references therein). Under certain conditions, the rate of spontaneous recombination of the coupled ''emitter-plasmon'' system can be increased above that of an isolated emitter, owing to a significant local increase in the photonic mode density near the metallic surface. This effect, which is in many aspects equivalent to the Purcell effect, has been detected for single organic molecules and colloidal QDs [7–9]. It appears very attractive to take advantage of this mechanism in order to improve the efficiency of the QD single-photon devices. However, to the best of our knowledge, the plasmonic enhancement has never been reported for a single emitter (a single QD or a single localized exciton) buried in a semiconductor epitaxial structure.

In this Letter we report on the strong local enhancement (more than an order of magnitude) of the emission of individual localized excitons in an InGaN film due to their coupling to a gold-nanoparticle plasmon. The particle is attached to an atomic force microscope (AFM) probe that allows its precise location in the near field of the surface. The effect of the recombination-rate increase in the InGaN/Au system is proved by time-resolved studies of the films with deposited Au clusters.

We focus on the $In_xGa_{1-x}N$ films, where the spectral coincidence of the emission line with the plasmonic resonance can be realized by variation of the In content. These films are deposited by plasma-assisted molecular beam epitaxy on *c*-plane sapphire above a GaN buffer. N-rich growth conditions result in a nanocolumnar film morphology with the characteristic surface roughness on the scale of 100 nm (see Fig. 1). This roughness permits flexible positioning of the plasmonic particle with respect to the direction of the exciton dipole moment. A strong localization of excitons takes place in the films with high enough content of In due to compositional fluctuations. The emission spectrum of such films is usually strongly inhomogeneous. As an example, Fig. 2 presents low-temperature cw spectra of photoluminescence (PL) and PL excitation (PLE) recorded in a 200 nm thick film with $x = 0.25$. An excitonic peak is well visible in the PLE spectra. The energy of this peak noticeably depends on the detection energy, which suggests that we selectively measure the PLE spectra of different groups of excitons localized in

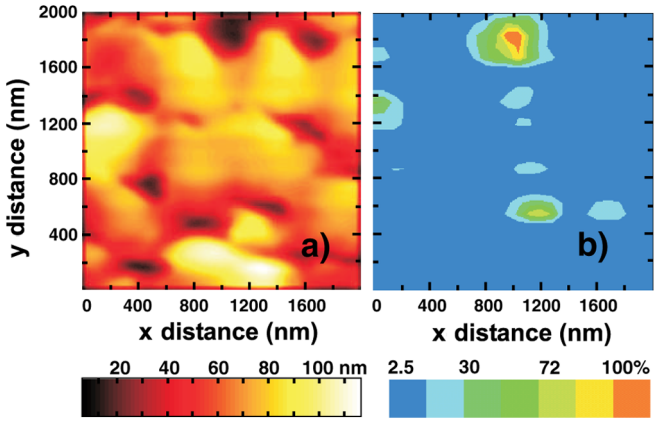

FIG. 1 (color online). Topographical (a) and TEPL (b) images simultaneously measured in the same spot of an $In_{0.25}Ga_{0.75}N$ film at 295 K. The intensity-color calibration of the image in (b) is specified as a percentage of the maximum PL intensity detected within the image.

different areas within a 0.5-mm excitation spot. For the long-wavelength tail of the band the exciton localization energy is as large as 400–500 meV. In many aspects they can be regarded as 0-dimensional excitons in a QD. The spectral range of the emission of the localized excitons in general overlaps with the plasmonic resonance in a gold sphere.

The basic experiments were carried out with a low-temperature near-field scanning optical microscope (NSOM) system (Nanonics CryoView 2000). Both the illumination of the sample and PL detection were performed via a confocal optical microscope with a 50× objective. The device was operated in a tapping-contact mode. During the near-field scans, the tip and illumination were fixed, while the sample was scanned in two directions by a piezoelectric element. This allowed the simultaneous acquisition of a topographical (AFM) image and an image of tip-enhanced PL (TEPL). A 532 nm cw laser line was used as an excitation. The respective quantum energy is

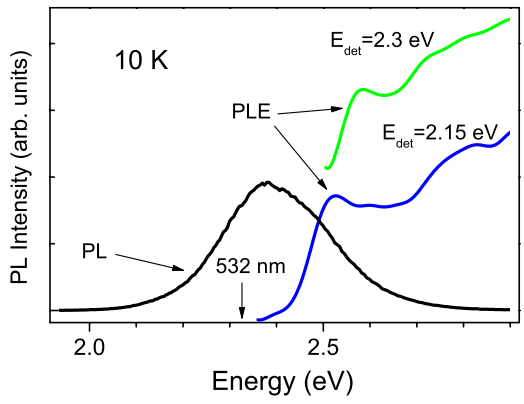

FIG. 2 (color online). PL and PLE spectra measured in an $In_{0.25}Ga_{0.75}N$ film at 10 K with excitation by a 325 nm laser line and the light of a tungsten lamp dispersed by a monochromator, respectively.

below the excitonic resonance in the PLE spectra, and only deeply localized excitons can be excited resonantly (see Fig. 2). The spectra of the collected light were recorded by a 30 cm spectrometer equipped with a cooled CCD camera. The PL enhancement was observed using AFM tips produced from glass fibers with an attached single gold nanoparticle. The characteristic size of the particle was in the range of 100–200 nm. We have also checked the AFM probes of other types: glass fiber tips covered by chromium and aperture NSOM fiber tips covered by either chromium or gold. No PL enhancement was observed with any of these probes.

Figure 1 shows topographical [Fig. 1(a)] and TEPL [Fig. 1(b)] images measured in an arbitrary place of the $In_{0.25}Ga_{0.75}N$ film at 295 K. The illumination spot size was $\sim 2\ \mu$m. The image in Fig. 1(b) is the map of the PL intensity integrated between 577 and 603 nm. This range corresponds to the maximum of the emission line and represents one frame of the used CCD detector. The TEPL image consists of bright spots with typical sizes 100–300 nm, which are 1–2 orders of magnitude brighter than the surrounding background. Comparing Figs. 1(a) and 1(b), one can notice certain correlation between the surface topography and TEPL signal. The most intensive "bright" spots tend to emerge within the pits of the topographic relief rather than protrusions. Generally, in order to observe a sizable enhancement, the emitting dipole should be oriented normally to the surface of the plasmonic particle [10–12]. This condition cannot be efficiently fulfilled in the geometry of a confocal optical microscope, if the particle is just placed above the flat surface of a layer containing QDs. However, when the plasmonic nanoparticle is positioned within the pit and the amplified exciton is localized somewhere in the film surrounding this pit, the optimal configuration for the detection of the plasmonic amplification can be realized. Similar experiments were performed with various $In_xGa_{1-x}N$ films ($0.2 < x < 0.5$). The tip-induced enhancement of the emission of localized excitons was readily observed in all these samples. The density of bright spots in the TEPL images in different samples was in the range of 1–10 μm^{-2}. It correlated roughly with the density of pits that are large enough to accommodate the gold particle.

Figure 3(a) shows the PL map measured at the same place and in the same conditions as the TEPL image in Fig. 1(b), except that the AFM probe was driven far away from the place of measurements. This PL image is also inhomogeneous; however, the observed intensity pattern does not correlate with the pattern of TEPL in Fig. 1(b). It reflects rather the inhomogeneity within the excitation spot, induced by notch interference filters used in the NSOM system. Comparing the images in Figs. 1(b) and 3(a), one can notice that the effect of the tip-induced enhancement is more than 1 order of magnitude stronger than these instrumental modulations. The TEPL images, measured with the probes of different types, are basically similar to the PL image shown in Fig. 3(a). These obser-

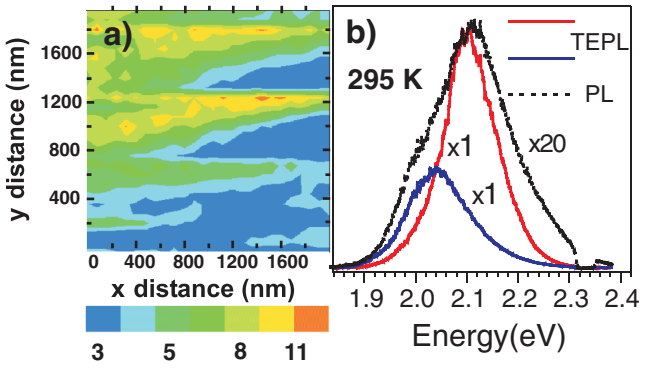

FIG. 3 (color online). (a) A micro-PL image measured with the retracted AFM probe at 295 K in the same area of the $In_{0.25}Ga_{0.75}N$ film as the image in Fig. 1(b) and with the same scale at the intensity-color calibration bar. (b) TEPL (solid lines) and PL (dotted line) spectra measured at 295 K. The PL spectrum in the plot is multiplied by 20.

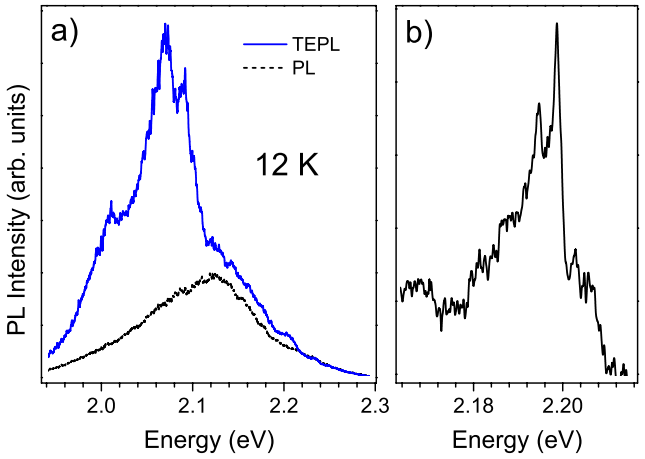

FIG. 4 (color online). (a) TEPL (solid line) and PL (dotted line) spectra measured in the $In_{0.25}Ga_{0.75}N$ film at 12 K. (b) A TEPL spectrum with narrow excitonic lines, obtained by fine-tuning of the tip position.

vations have allowed us to identify the observed strong PL enhancement as an effect of the gold particle attached to the AFM probe.

To specify the action of the particle, we present in Fig. 3(b) the PL spectrum (dotted line) measured at 295 K at a certain point of the $In_{0.25}Ga_{0.75}N$ film and two TEPL spectra (solid lines) measured with the probe set in the near-field regime at different locations within the same excitation spot. In this experiment the sample position and the illumination were fixed, while the probe was precisely located by a piezoelectric element within a certain pit of the topographic relief. The approach of the tip to the surface results in a drastic local enhancement and narrowing of the PL line. In the optical microscope it looks like an appearance of a bright orange point with diffraction-limited sizes. This behavior can be understood as the selective enhancement of a part of the inhomogeneously broadened emission spectrum by affecting only a limited number of localized excitons. To go beyond the temperature-induced broadening we measured similar spectra at 12 K [see Fig. 4(a)]. The typical TEPL spectrum consists of a number of lines with different spectral width. For some places on the sample surface, an accurate positioning of the tip results in appearance of the emission lines as narrow as 1.5–2 meV that is the spectral resolution of the used spectrometer [see Fig. 4(b)]. These narrow lines resemble the emission spectrum of single localized excitons in InGaN QDs measured in the similar conditions [13]. We believe that this observation is relevant to the tip positioning at the local place, where the density of localized excitons is accidentally smaller than the average value.

Previously, the amplification effect of an AFM conducting tip was discussed in terms of two different mechanisms caused by the local increase of the photonic mode density. The PL enhancement can occur due to either the local increase of the exciting electromagnetic field or the increase of the spontaneous emission recombination rate [8,9]. It is not easy to distinguish reliably between them. In most of the previous measurements, the tip was directly illuminated either sideways or through a transparent substrate [14]. Hence, the electromagnetic mechanism was believed to be essential. In contrast to the previous studies, we use the top-illumination geometry, when the shadowing of the gold nanoparticle by the glass part of the AFM probe can prevent direct coupling of the external electromagnetic field to the plasmonic modes. Thus the recombination-rate mechanism can be essential in the effect of the tip-induced PL enhancement.

A confirmation of the dominant role of such a type of enhancement was obtained by measuring a temperature dependence of the amplification factor. The increase of the temperature enhances the rate of the nonradiative recombination due to ionization of the localized carriers and their transport towards defects. The resulting amplification should depend on the relationship between the rates of the radiative and nonradiative recombination. The stronger the nonradiative channel, the higher amplification by the recombination-rate mechanism may be achieved. On the contrary, the intensity of the exciting electromagnetic field should not noticeably depend on the rate of the nonradiative recombination, and the respective contribution to the amplification factor should be independent of the temperature. The observed strong enhancement of the amplification factor with the rise of temperature [compare the spectra in Figs. 3(b) and 4(a), measured at nearly the same place of the sample] is consistent with the dominance of the rate-controlled mechanism.

To elucidate further the nature of the enhancement we have performed a complementary study of recombination dynamics after the excitation by a subpicosecond laser pulse both in the as-grown $In_{0.25}Ga_{0.75}N$ film and in the film covered with a small amount of Au (the effective gold thickness was ~20 nm). Because of the roughness of the InGaN surface, the deposited metal forms clusters (islands), which are situated predominantly in the pits. Thus

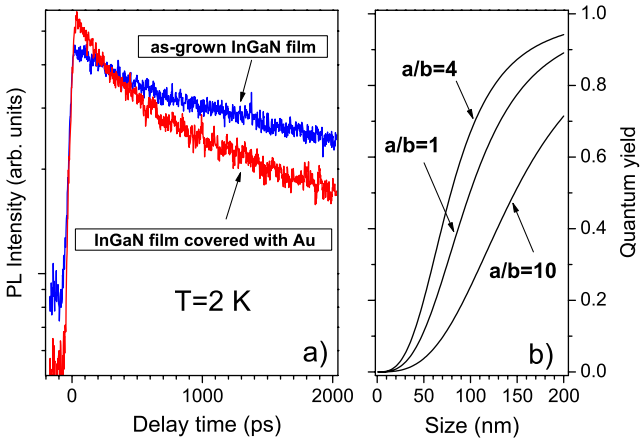

FIG. 5 (color online). (a) Decay curves of PL recorded at 530 nm either in the as-grown InGaN film or in the film covered with Au. (b) Quantum yield of a gold spheroid, calculated versus length of the semimajor axis a for different a/b ratio.

there was certain similarity between the plasmons localized in these islands and in the gold nanoparticle attached to the AFM tip. The emission with an enhanced decay rate is observed in the Au-covered film in the spectral range of the plasmonic resonance [Fig. 5(a)], which confirms the rate-controlled mechanism of the PL enhancement. It is essential that the decay shortening is accompanied by an increase in the emission intensity at short delays, that means that the enhancement overcomes the optical losses in the gold covering.

The observation of the enhancement effect implies that the radiative decay rate of the particle plasmon (Γ_r) should prevail over the nonradiative energy dissipation (Γ_{nr}) in the metal particle. In other words, the quantum yield, defined as

$$Y = \Gamma_r/(\Gamma_r + \Gamma_{nr}), \tag{1}$$

should be reasonably large. The emission yield of an excited metal spheroid with its semimajor and semiminor axes a and b, respectively, can be estimated as [10]

$$Y = \left\{1 + \frac{9}{2}\left(\frac{c}{\omega f}\right)^3 \mathrm{Im}(\epsilon)\left(\frac{\xi_0^2 - 1}{\xi_0}\right)[Q_1(\xi_0)]^2\right\}^{-1}, \tag{2}$$

where $f = (a^2 - b^2)^{1/2}$, $\xi_0 = a/f$, c is the light velocity in vacuum, ϵ is the metal dielectric function, and ω is the plasma resonant frequency. $Q_1(\xi_0)$ is a Legendre function of the second kind. It is assumed that the spheroid has been excited in a dipolar mode with the dipole oscillating parallel to the major axis. The quantum yield increases with a [see Fig. 5(b)] and depends nonmonotonously on the a/b ratio. The highest quantum yield corresponds to $a/b \sim 4$ ($\omega \sim 2.0$ eV) that matches the absolute minimum of the imaginary part of the dielectric function of gold. The gold sphere ($a/b = 1$) with the characteristic size ~150 nm corresponds to the very boundary of the region of the efficient plasmonic emission. Note that the increase of a/b improves the spatial resolution of the method.

On the basis of these data we propose the following description of the plasmonic enhancement under the conditions of top illumination. The external field creates excitons which populate the sites of localization in the vicinity of the tip. The exciton emission dipole couples to the macroscopic dipole in the metal particle. The induced polarization is resonantly enhanced near the frequency of the electronic plasma resonance, that results in a concomitant increase in the radiative emission rate of the total dipole. Several circumstances are needed for the efficient amplification of the excitons emerging at the near-field distance from the gold particle. First, the excitonic transition should be properly polarized and possess a resonant frequency near the plasma resonance. Then, the exciton should suffer from a nonradiative damping. And finally, the radiative decay rate of the plasmon should prevail over the nonradiative energy dissipation.

Summarizing, we have demonstrated effective control over the recombination efficiency of individual excitons localized in inorganic semiconductor structures, namely, InGaN films. A gold plasmonic nanoparticle serves as an amplifier of a local photonic mode density for a number of excitons, which are at the near-field distance. We believe that this approach is promising as a relatively simple way to extract the radiation of a single quantum emitter operating at elevated temperatures.

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[1] P. Michler *et al.*, Science **290**, 2282 (2000).
[2] C. Santori *et al.*, Nature (London) **419**, 594 (2002).
[3] E. M. Purcell, Phys. Rev. **69**, 681 (1946); D. Kleppner, Phys. Rev. Lett. **47**, 233 (1981).
[4] S. Kako *et al.*, Nature Mater. **5**, 887 (2006).
[5] K. Sebald *et al.*, Appl. Phys. Lett. **81**, 2920 (2002).
[6] W. L. Barnes, J. Mod. Opt. **45**, 661 (1998).
[7] A. V. Akimov *et al.*, Nature (London) **450**, 402 (2007).
[8] J. R. Lakowicz, Anal. Biochem. **298**, 1 (2001).
[9] J. N. Farahani *et al.*, Phys. Rev. Lett. **95**, 017402 (2005).
[10] J. Gersten *et al.*, J. Chem. Phys. **75**, 1139 (1981).
[11] D. A. Weitz *et al.*, J. Chem. Phys. **78**, 5324 (1983).
[12] V. V. Klimov *et al.*, Chem. Phys. Lett. **358**, 192 (2002).
[13] A. F. Jarjour *et al.*, Appl. Phys. Lett. **91**, 052101 (2007).
[14] H. F. Hamann *et al.*, J. Chem. Phys. **114**, 8596 (2001); H. G. Frey *et al.*, Phys. Rev. Lett. **93**, 200801 (2004); J. M. Gerton *et al.*, Phys. Rev. Lett. **93**, 180801 (2004).