Exciton localization in ultradilute Ga(As,N) investigated by means of near-field autocorrelation spectroscopy

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We report on low-temperature near-field photoluminescence (PL) spectroscopy of ultradilute Ga(As,N) layers with only 0.1% nitrogen. Near-field PL spectra are dominated by ultranarrow emission spikes from single excitons localized in local minima of the band gap potential arising from fluctuations of the nitrogen concentration. The two-energy autocorrelation function of such spectra shows a distinct shoulder at energies below 1 meV, which is a signature of level repulsion between neighboring localized excitons. An analysis based on a statistical disorder model allows to estimate both the amplitude (few meV) and the correlation length (about 20 nm) of the disordered potential. The results indicate that local band gap fluctuations on a length scale of roughly the exciton Bohr radius dominate the optical properties of even ultradilute Ga(As,N) films.

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Incorporating small amounts of nitrogen into GaAs and (In,Ga)As causes a substantial band gap reduction [1–3]. This giant band bowing effect has led to extensive studies of the optical properties of the Ga(As,N) and (In,Ga)(As,N) materials, as it allows one to control the band gap in a range of 1.4 – 0.8 eV. This makes such materials promising candidates for laser diodes in the important telecommunication wavelength range of 1.3 – 1.55 μm [4–6]. Many of the optical properties of these materials still remain to be understood and optimized. For example, the microscopic nature of defects that are created when incorporating nitrogen into GaAs and (In,Ga)As is still contentious [7–10]. Great efforts are currently being made to improve optical properties by an ex-situ thermal treatment [11–14]. Also, the effect of the nitrogen concentration on the effective electron mass is under scrutiny [15, 16]. One of the most important problems is to understand how local variations in the band gap profile affect the optical properties. Due to the large band bowing, these band gap fluctuations arise in Ga(As,N) and (In,Ga)(As,N) systems mainly from alloy disorder, i.e., slight spatial inhomogeneities of the nitrogen concentration in which excitons may be spatially localized [17–19].

In this Letter, we investigate the optical properties of thin, ultradilute Ga(As,N) layers using a novel technique, near-field autocorrelation spectroscopy [21, 22]. Based on a statistical analysis of local near-field optical spectra we demonstrate that alloy disorder in samples with 0.1% nitrogen results in exciton localization in shallow local minima of a random disorder potential with a correlation length of roughly 20 nm.

We investigate a 100 nm thick Ga(As,N) layer with 0.1% nitrogen grown by solid-source molecular beam epitaxy on a (001) GaAs substrate. Nitrogen was supplied by an ADDON RF plasma source. Prior to the Ga(As,N) growth, a 400 nm GaAs buffer layer was deposited at 550°C. The Ga(As,N) film was subsequently grown at 450°C at a rate of 0.13 monolayers per second. Finally, the sample was capped with 50 nm GaAs grown at 450°C. Ex-situ annealing was accomplished in a nitrogen atmosphere at 900°C for 60 s in order to remove grown-in defects. The sample was studied by low temperature near-field scanning optical microscopy (NSOM) at a sample temperature of $T = 10$ K [21, 23]. The experiments were performed in an illumination/collection geometry with a spatial and spectral resolution of 200 nm and 60 μeV, respectively. Light from a Helium-Neon laser (1.96 eV) was transmitted through a chemically etched, uncoated near-field fiber probe. The photoluminescence (PL) from the sample was collected in reflection geometry through the same fiber probe, dispersed in a 0.5 m monochromator, and detected by a liquid nitrogen cooled charged coupled device, as illustrated in Fig. 1 (a).

Figure 1 (b) depicts a spatially averaged PL spectrum of the Ga(As,N) sample, recorded at a low excitation power of 80 nW. The spectrum was obtained by averaging 1600 individual NSOM spectra taken by scanning a 6×6 μm^2 area in 150 nm steps. The emission peaks at 1.45 eV, i.e., 70 meV below the GaAs band gap. It is also red shifted with respect to the band gap position of $GaN_{0.001}As_{0.999}$ of 1.49 eV, predicted by the band anticrossing (BAC) model [20], which ascribes the band gap shift in this material to an electronic coupling between the conduction band and an energy band formed by nitrogen electronic states [2, 3]. This pronounced shift for such a small nitrogen concentration is related to a rather strong localization of excitonic states. Clear evidence for this localization comes from the individual NSOM spectra in Fig.1(c). In contrast to the averaged

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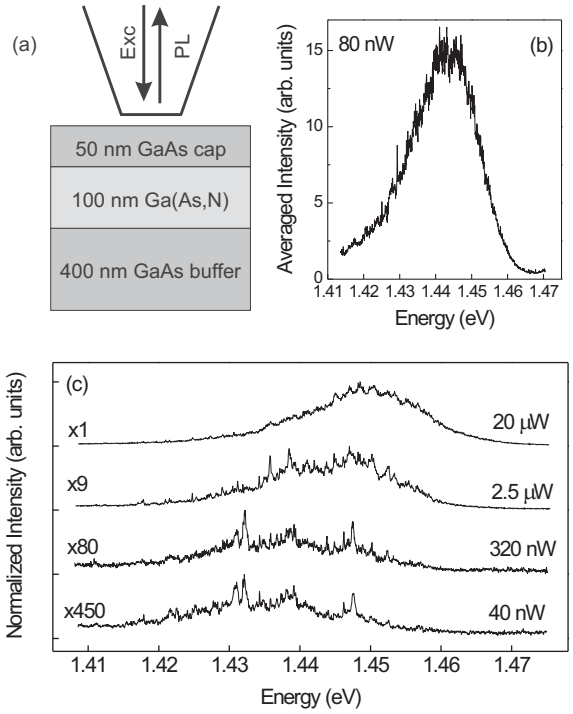

FIG. 1: (a) Schematic of the experimental setup. (b) Spatially averaged PL spectrum of the $GaAs_{0.999}N_{0.001}$ sample at $T = 10$ K, taken from 1600 NSOM spectra. (c) Individual near-field PL spectra recorded for different excitation powers at the same spot of the sample.

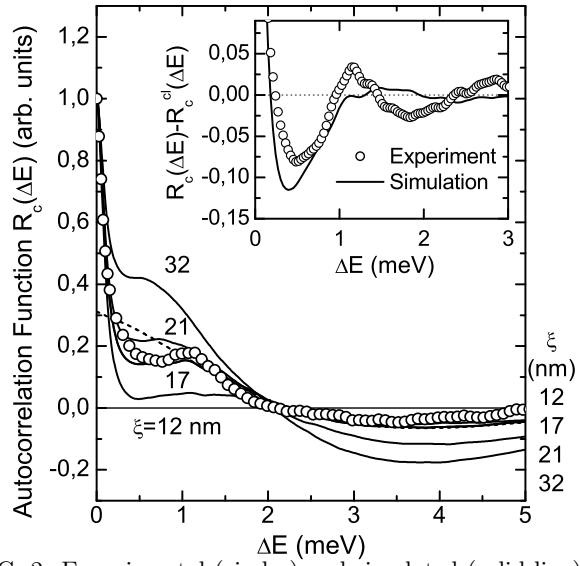

FIG. 2: Experimental (circles) and simulated (solid line) autocorrelation functions $R_c(\Delta E)$. The simulations were performed for a disorder amplitude of 2.1 meV and correlation lengths ξ of 12−32 nm. Dashed line: Classical limit ($M \to \infty$) for $\xi = 17$ nm. Inset: Deviation between experimental (circles) and simulated (line) data and the classical limit.

emission, the individual spectra break up into a series of spectrally sharp emission spikes from single localized excitons within the disordered potential created by the random fluctuations in nitrogen concentration. At low power, the intensity of the sharp spikes varies linearly with excitation power, whereas one observes a broadening of these lines and a clear blueshift of the PL spectrum at high power [Fig. 1(c)]. This blueshift reflects the filling of localized low energy states and the increasing occupation of and emission from higher states at a power above 1μW. Simply counting the average number of emission spikes in the PL spectra provides a rough estimate of the density of localized exciton states of about 5000 μm^{-3}.

A more quantitative understanding of exciton localization in ultradilute Ga(As,N) can be obtained from a statistical analysis of such near-field PL spectra. The idea behind this analysis is the following. Due to the quite large exciton Bohr radius of about 10 nm [17] and the high density of defect sites, a spatial overlap of the center-of-mass wave functions of two excitons in neighboring localization sites is likely. The energies of such states with overlapping wave functions are necessarily nondegenerate (level repulsion) [21, 24]. This means that the probability of finding two nearly degenerate emission spikes in a spatially resolved near-field spectrum is smaller than in the spatially averaged spectrum. This level repulsion shows up as a clear anticorrelation signature in the two-energy autocorrelation function of local near-field spectra [21, 22, 24]. This level repulsion dip gives information on both the amplitude and the correlation length of the disordered potential. The two-energy autocorrelation function [21, 24] is defined as:

$$R_c(\Delta E) = R(\Delta E) - R_0(\Delta E), \tag{1}$$

where $R(\Delta E)$ and $R_0(\Delta E)$ are defined by:

$$R(\Delta E) = \left\langle \int dE' I_n(E') I_n(E' - \Delta E) \right\rangle \tag{2}$$

$$R_0(\Delta E) = \int dE' \left\langle I_n(E') \right\rangle \left\langle I_n(E' - \Delta E) \right\rangle . \tag{3}$$

Here, $I_n(E)$ represents the intensity of the nth local optical spectrum. The brackets $\langle ... \rangle$ denote the ensemble average over many individual measurement spots. The experimentally measured values of the autocorrelation function are shown as open circles in Fig. 2. $R_c(\Delta E)$ is derived from an ensemble of 1600 NSOM PL spectra, recorded at an excitation power of 80 nW. The clear shoulder visible at energies between 0.3 and 1 meV is the experimental signature of excitonic level repulsion in the investigated Ga(As,N) layer.

To gain quantitative insight into the disorder potential, one should compare the experimentally measured $R_c(\Delta E)$ to a numerical simulation.Ideally, near-field PL spectra should be simulated based on a realistic description of the three-dimensional disorder potential induced by the local fluctuations in nitrogen content. Also, the exciton relaxation dynamics should be taken into account. Such simulations are beyond the scope of this paper as they are numerically highly demanding and have

- so far - only been performed for a one-dimensional model quantum wire structure [25]. Instead, we consider a two-dimensional disorder potential with amplitude σ and correlation length ξ [21, 24]. Local absorption spectra are calculated by solving the two-dimensional Schrödinger equation for 1000 random realizations of the disorder potential. An effective center-of-mass exciton mass $M = 0.5m_0$, m_0: electron mass, is assumed. The quantities (1) - (3) are determined by performing the appropriate ensemble averaging. To account for the finite linewidth of the individual spikes, the results are convoluted with a Lorentzian of width $2\gamma = 0.1$ meV. The value of σ is obtained by fitting to the high-energy region with negative values of $R_c(\Delta E)$. Then, ξ is chosen to best reproduce the level repulsion shoulder. Simulated $R_c(\Delta E)$ curves for different values of ξ are compared to the experimental data in Fig. 2. From this procedure, we obtain $\sigma = 2.1 \pm 0.5$ meV and $\xi = 17 \pm 4$ nm.

The level repulsion anticorrelation becomes evident by comparing experimental and theoretical $R_c(\Delta E)$ to the so-called "classical" autocorrelation function $R_c^{cl}(\Delta E)$, calculated in the limit of an infinitely large exciton mass $M \to \infty$. In $R_c^{cl}(\Delta E)$ (shown for $\xi = 17$ nm as a dashed line in Fig. 2), level repulsion effects are absent. Level repulsion results in the pronounced negative values of $R_c(\Delta E) - R_c^{cl}(\Delta E)$ in the range between 0 and 1 meV (inset in Fig. 2).

The observed value of $\sigma = 2.1$ meV appears - at first sight - surprisingly small. Several authors have reported on potential fluctuations between 40 and 60 meV in different Ga(As,N) alloys [19, 26]. This apparent discrepancy may be rationalized by considering that previous studies have been performed on samples with a higher N content, where disorder is more pronounced due to the stronger band bowing. In addition, they investigated mostly weakly localized, more extended exciton states [23], giving rise to the broad background in the near-field spectra (A band in Ref. [19]). Our experiments, however, probe strongly localized excitons, giving rise to the sharp emission spikes. Also in Ref. [19] it is seen that the emission from most of the sharp spikes vanishes around temperatures of only $20 - 40$ K, corresponding to a thermal activation energy of $2 - 3$ meV.

The correlation length of $\xi = 17$ nm points to a density of localization sites of roughly 10^4 μm^{-3}. This is in fair agreement with the estimate based on the number of emission spikes and also with a previous estimate of $100-1000$ μm^{-3} for Ga(As,N) samples with $1-3$% nitrogen [19]. The exact value of ξ should certainly be taken with some care, as it is based on an oversimplified two-dimensional model neglecting exciton relaxation effects. Yet, the quite pronounced level repulsion signature in the experimental data indicates that near-field autocorrelation spectroscopy is a powerful means of obtaining quantitative information on alloy disorder in Ga(As,N) based materials. In particular, we expect that this correlation feature is highly sensitive to variations in nitrogen content and annealing conditions, making it interesting to extend this work to a broader range of samples. Also, we point out that, in these materials, it should be possible to probe localization more directly by local linear or nonlinear absorption spectroscopy [27]. This would greatly simplify the quantitative comparison to theory.

In summary, low temperature near-field photoluminescence spectroscopy gives evidence for exciton localization even in ultradilute Ga(As,N) films. By means of a statistical analysis of the two-energy autocorrelation function of such spectra, we provide estimates for both the amplitude and the correlation length of the disorder potential induced by random spatial fluctuations of the nitrogen concentration. We anticipate that these results will stimulate further theoretical studies of exciton localization in Ga(As,N)-based structures as well as experimental studies of the effects of both nitrogen concentration and thermal annealing treatments on the optical properties of this technologically relevant class of materials.

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