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Exciton and Biexciton Luminescence from Single GaN/AlN Quantum Dots in Nanowires

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ABSTRACT

We present a microphotoluminescence study of single GaN/AlN quantum dots embedded in single nanowires. At low excitation power, single exciton lines with full width at half-maximum as narrow as 1 meV are observed. The study of the excitation power dependence of the emission allows us to identify the biexciton transitions with binding energies ranging from 20 to 40 meV.

GaN/AlGaN heterostructures present an interesting potential for optoelectronics applications such as ultraviolet (UV) emitters or telecommunication wavelength intersubband devices. Single GaN quantum dots could also be used to demonstrate single photon emission at room temperature due to large band offsets between GaN and AlN. Such GaN/AlGaN heterostructures present a fundamental interest due to their peculiarities: when grown along the *c* axis, they exhibit a huge internal electric field as a consequence of the wurtzite structure.[1] Furthermore, the large band offsets and the large hole effective mass lead respectively to strong confinement and localization effects. Single polar GaN/AlN quantum dots grown by metal−organic chemical vapor deposition[2] and by molecular beam epitaxy (MBE),[3] as well as nonpolar GaN/AlN quantum dots grown by MBE,[4] were experimentally studied by microphotoluminescence. In these quantum dots grown in the Stranski−Krastanow (SK) mode, the quantum dot density is difficult to master; defects in the structure lead to residual emission in the quantum dot emission spectral region and to strong spectral diffusion effects. Concurrently, nanowire geometry appears as a solution to achieve high crystal quality in III−N material.[5,6] Therefore, defect-free GaN quantum dots based on nanowire heterostructures are expected to be achieved and to overcome the limitations occurring in the case of SK quantum dots. Using a longitudinal heterostructure in a nanowire is one promising way to study single GaN/AlN quantum dots and possibly use them for optoelectronics applications. Indeed in MBE, GaN grows naturally as nanowires under N-rich conditions.[5,6] Making quantum dots in a nanowire[7] is a new way to fabricate and study these heterostructures that allows in particular to easily isolate one and only one quantum dot for optical studies, and in the particular case of GaN structures, allows to get rid of residual emission stemming from the matrix that is usually observed for SK quantum dots. So far, the MBE growth of GaN and AlGaN nanowires has been demonstrated.[6,8] GaN nanowires reveal excellent optical properties in comparison with bulk GaN, mainly due to the absence of defects in nanowires.[6,9] The growth of GaN insertions inside AlGaN nanowires has been achieved.[10] However, these structures reveal a very broad (more than 100 meV) emission arising from the insertions even on a single wire.[10,11] We demonstrate in this article a narrow emission (down to 1 meV) of single GaN/AlN quantum dots in nanowires and identify the excitonic and biexcitonic recombinations of these quantum dots.

To create GaN/AlN insertions, first GaN nanowires are grown on Si(111) substrate under N-rich atmosphere by using plasma-assisted MBE. In our case, a thin two-dimensional (2D) AlN buffer layer was grown prior to GaN deposition on Si substrate in order to improve the wire orientation.[12] The nanowires grew along the *c* axis which is the polar direction of the wurtzite structure. After the growth of GaN nanowires, we deposited an AlN barrier followed successively by a GaN insertion and a top AlN barrier. The structural properties of GaN quantum dots were investigated by high resolution transmission electron microscopy (HRTEM).

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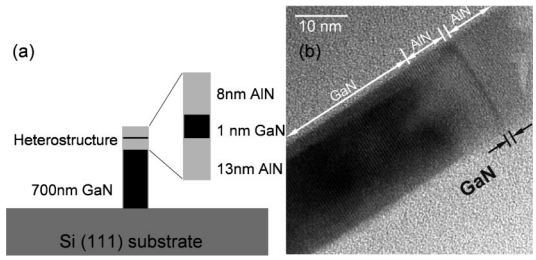

Figure 1. (a) Schematic illustration of GaN/AlN inclusions on the top of GaN nanowires grown on Si (111) substrate. Note that the schematic is not to scale. (b) HRTEM image of a single GaN/AlN inclusion.

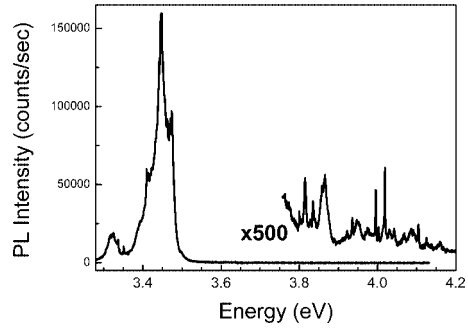

Figure 2. Microphotoluminescence spectrum of an ensemble of GaN nanowires with GaN/AlN insertions at 5 K. The excitation power is 10 μW.

We studied the optical properties of the wires by continuous wave microphotoluminescence at low temperature (5 K). We used the frequency-doubled line ($\lambda = 244$ nm) of an argon laser for the excitation. The diameter of the excitation spot is about 1 μm. The collected light was dispersed by a 55 cm focal length monochromator together with a 1200 grooves/mm grating and detected by a UV-enhanced nitrogen-cooled charge-coupled device (CCD). The setup spectral resolution is about 500 μeV at a detection wavelength of 350 nm.

Figure 1a schematically illustrates the structure investigated in our experiments. One nanometer thick GaN inclusions embedded in 13 and 8 nm AlN barriers are located at the top of 700 nm long GaN wires. The nanowire diameters are in the range of 20−40 nm, and the density is in the range of 200 wires μm^{-2}. The GaN inclusions are radialy surrounded by ~1 nm AlN, as illustrated in the HRTEM image in Figure 1b. This is attributed to a significant lateral growth rate of AlN.[9,13]

The GaN "quantum dot" in the wire is thus a disk about 1 nm thick and 30 nm in diameter in an AlN matrix. These dimensions are to be compared with the Bohr radius in GaN which is 2.8 nm.[14] The carriers will hence be strongly confined along the longitudinal direction, while it is expected that the confinement in the layer plane will be weak, leading to a center of mass confinement of a 2D exciton.

In Figure 2, we present a microphotoluminescence spectrum obtained on an as-grown sample. In that case, the optical excitation and detection are made along the longitudinal direction of the wires. The intrinsic absence of wetting layer for dots embedded in nanowires suggests that the excitation (5.08 eV) occurs directly in a quasi continuum of excited states of the dots. Because of the large nanowire density, the luminescence from a few 100s of nanowires is collected. The dominant emission is a GaN near band edge signal (luminescence below 3.5 eV) which is attributed to the large amount of GaN localized at the lower part of the wire. The much weaker signal with very sharps lines (down to 1 meV line width) at high energy stems from the single GaN insertions. We checked that this emission is indeed due to the GaN insertions by growing a control sample in which the GaN nanowires are only capped by AlN that does not contain GaN insertions. Under the exact same optical experiment conditions, the sample without the insertions does not show any detectable signal in the energy range where the sample with insertions emits. The large dispersion in the emission energy of GaN quantum dots is consistent with large height dispersion for these structures. For such quantum dot diameters and height, the lateral confinement contributes negligibly to the transition energy and the internal electric field does not play a significant role.[15] Therefore, a simple realistic model for calculating the transition energy of such quantum dots is to consider a "field free" GaN/AlN quantum well. It shows that around 1 nm, a variation of only 1 monolayer in the confinement direction results in a 200 meV shift in the emission energy. It has been shown that the GaN nanowire growth is limited by the diffusion of Ga.[12] The quantum dot height fluctuation might then arise from the growth competition among neighboring nanowires which results in different vertical growth rate of nanowires and consequently, inhomogeneity of quantum dot height. We note that the near band edge emission is quite broad and presents different peaks and that its contribution extends significantly down to 3.2 eV. The complexity of the near band edge signal is attributed to the AlN layers laterally capping the GaN wires. We indeed did not observe such under band gap extension of the near band edge signal for standard GaN wires. The effect of the AlN capping is likely due to its significant lateral growth which induces strain and possibly defects at the GaN/AlN lateral interfaces.

To investigate single quantum dot emission, we removed nanowires from their substrates by sonication and dispersed them onto Si substrates. In this configuration, excitation and collection are made in the radial direction of the wires. In Figure 3, we present typical spectra obtained from a single wire at low excitation power of about 500 W cm^{-2}. Apart from a strong near band edge signal (not shown), we observe quantum dot emissions at much higher energy in the range from 3.8 to 4.2 eV, consistently with the photoluminescence from nanowires ensemble. Let us note that most often a near band edge signal is observed with no quantum dot emission. Furthermore, another significant part of the emitting dots presents a rather broad emission (more than 10 meV). It thus results that only a few percent of the quantum dots in the nanowires emit an intense enough and spectrally narrow photoluminescence signal. We also stress that, in Figure 3, the spectra are taken at low excitation power. We indicated the count rate we get as an indication (one CCD-pixel for 250 μeV). As we do not know what is the far field emitted

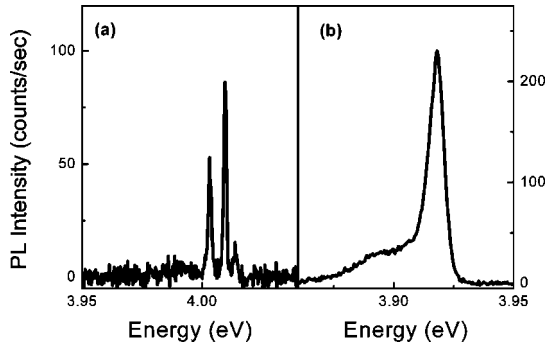

Figure 3. Microphotoluminescence spectrum at 5 K of two different single nanowires dispersed on a Si substrate. The excitation powers are 10 μW (a) and 5 μW (b).

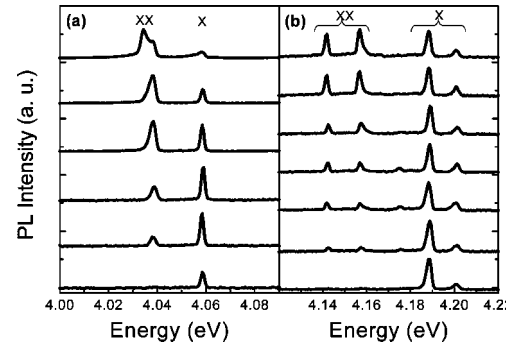

Figure 4. Power-dependent spectra of quantum dots emissions at 5 K. Each spectrum has been normalized to its maximum intensity. Excitation powers (increasing from the bottom): 10, 50, 100, 200, 300, and 500 μW for (a) and 25, 100, 120, 170, 200, 250, and 300 μW for (b).

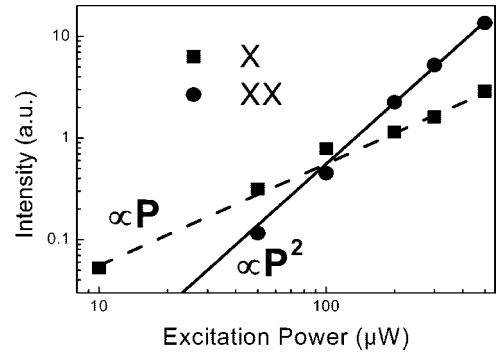

Figure 5. Dependence of the energy-integrated photoluminescence intensity of the lines labeled X (exciton) and XX (biexciton) in Figure 4a as a function of the excitation power on a log−log scale. The solid lines represent a linear and a quadratic dependence.

by our emitters in our particular electromagnetic configuration (one nanowire lying on a high index substrate, the emitter most likely having a dipole perpendicular to the wire axis), we are not able to evaluate the photon collection efficiency we have in this particular experiment. Two distinct behaviors were commonly observed: either a single line (Figure 3b) or a multiplet (Figure 3a). In both cases, the lines show a linear dependence on the excitation power and are hence attributed to single electron−hole pair recombination. The single line or multiplet observed in the low excitation power limit will thus thereafter be called the "excitonic line(s)". In the case of multiplets, the several lines are attributed to the time dependent presence of trapped carriers very close to the dots or to carriers inside the dots (charged excitons). The full width at half-maximum (fwhm) of these lines varies between 1 and 10 meV. Generally, when observing a multiplet, the linewidths are smaller. A broad single line could actually be composed of several lines shifting from one to the other at high frequency compared with our integration time (a few seconds) if the trap density is large enough.[3] Let us compare the features of these excitonic lines with what has been reported in the literature for single GaN/AlN SK quantum dots. The linewidths are comparable with the commonly measured values on c-plane GaN/AlN SK quantum dots.[2,3] The large linewidths and multiplets in GaN/AlN c-plane SK quantum dots are attributed to the presence of defects that trap and detrap carriers.[3] Our spectra of single dots in nanowires are background-free in contrast with SK dots which could be a strong advantage for performing correlations measurements and for the realization of single photon sources.[16] The background in SK dots possibly comes from neighboring dots and/or from substrate and buffer layer defects luminescence. The typical dots density in GaN/AlN SK dots is around 10^{10} cm^{-2}.[17,18] This makes, thus, the excitation of a single dot quite difficult. This is different for quantum dots embedded in nanowires for which the density can be reduced as much as wished by the nanowires dispersion.

We studied the power dependence of the single dot emission, as presented in Figure 4. As a general tendency, we observe the apparition of additional lines in the low energy part of the spectrum, typically between 20 and 40 meV below the excitonic lines. When acquiring several photoluminescence spectra successively, we can observe the spectral diffusion occurring on our acquisition time scale.[3] We can, in particular, correlate the temporal evolution of the low energy lines with the excitonic lines and thus attribute them to the same dots. In Figure 5, we plot the integrated photoluminescence intensity for the quantum dot studied in Figure 4a as a function of the excitation power over almost 2 orders of magnitude. Differing from the linear dependence observed in the case of the exciton line, the intensity of the low energy line shows a quadratic dependence on the excitation power suggesting a transition from a biexciton state to an exciton state with a binding energy around 20 meV for the biexciton. The highest power spectrum presents more complicated features with the appearance of a second line in the biexciton emission as well as a shoulder in the exciton emission. Both are likely related to charges trapped around the dot. In Figure 4b, we present photoluminescence spectra of a single quantum dot at different excitation powers showing several lines at low power. The additional lines appearing at higher power display a quadratic dependence of their intensities with the excitation power. We are thus in the presence of different charged states for the biexciton emissions as well as for the excitons. In this case, the biexciton binding energy is around 40 meV. Note that the expected saturation of the exciton lines, which should begin

when the biexcitonic emission starts to dominate the spectrum, is not observed. This fact is still unclear, and further studies are needed to address this problem.

So far for c-plane GaN/AlN SK dots, evidence for biexcitonic emissions were reported for larger dots emitting between 3.2 and 3.5 eV.[2,16] At these energies the effect of the internal electric field dominates the confinement resulting in a weak overlap of the electron and hole wave functions. Repulsive interactions between trapped carriers thus become stronger than the attractive ones, and as a consequence the biexciton binding energy has been observed to be negative with absolute values around 30 meV.[2,16] It was recently shown that the compensation of the internal electric field by an external field in InGaN/GaN dots leads to a larger electron and hole wave functions overlap, the consequence being an increase of the attractive Coulomb interaction and a change in the sign of the biexcitonic binding energy.[19] Recently, by studying GaN/AlN polar SK quantum dots with various heights, Simeonov and co-workers showed that both positive and negative biexciton binding energies could be observed depending on the quantum dot height.[20] For quantum dots that are 7 ML (1.8 nm) high and emit around 4 eV, they observe a positive binding energy of the biexciton around 2 meV. Our observations are the first report of a large positive biexciton binding energy in GaN/AlN quantum dots, consistent with the negligible effect of the electric field in these thin GaN quantum dots. The difference in binding energy between the findings of Simeonov and co-workers[20] and the results presented in this article require further experiments as well as modeling to assess the possible differences in confining potential between SK quantum dots and quantum dots in nanowires.

A first question that arises from this study refers to the origin of the poor luminescence yield of the GaN quantum dots. In our dispersed sample, most quantum dots do not emit; it is thus important to find out whether this is an intrinsic property of such nanowires or if the dispersion process (including interactions with the substrate) plays a role in this low emission yield. Another fundamental question is to understand whether the quantum confined Stark effect (QCSE) would play an important role in thicker quantum dots, in the same way as for SK GaN quantum dots. Indeed, the unambiguous signature of QCSE has not yet been reported in wurtzite nanowire heterostructures. This could be due to an intrinsic reduction of the internal field in nanowires. The limited lateral extent of the nanowires intrinsically reduces the size of the GaN/AlN interfaces that carry the sheet charge density induced by the polarization discontinuities, thereby reducing the internal electric field strength. Moreover, the large number of surface states as well as possible adsorbates on the lateral surface of the nanowire can contribute to the screening of the electric field. Further theoretical and experimental studies are required to precisely assert the possibility of having a sizable QCSE in such nanowire longitudinal heterostructures. In our particular case, the way to study the QCSE would be to grow larger inclusions (more than 2 nm in height) in which case the transition red shift and the decrease in the transition oscillator strength become a clear signature of an internal electric field.[21,22]

In conclusion, we have identified the excitonic and biexcitonic recombinations stemming from single GaN/AlN quantum dots embedded in nanowires. For such small quantum dots (around 1 nm height), we observed the low temperature emission energy above the band gap of GaN between 3.8 and 4.2 eV. The typical fwhm are in the range between 1 and a few meV, while the biexciton binding energy is between 20 and 40 meV. This unique quantum dot geometry provides an opportunity to study the physics of single GaN quantum dots, with the possibility to easily isolate a single quantum dot and with the absence of background emission. A key point to address is the role of the lateral AlN barrier capping on the electronic properties of these quantum dots, that is, its impact on the radiative efficiency and spectral diffusion. Because of their particular growth mode, these quantum dots in nanowires also open the path toward the realization of vertically coupled identical quantum dots. This first characterization of single GaN quantum dots in a nanowire is promising to get a better understanding and mastering of GaN/AlN heterostructures, as well as for potential applications such as UV emitters and room temperature single photon sources.

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