InGaN quantum dots with short exciton lifetimes grown on polar c-plane by metal-organic chemical vapor deposition

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Abstract
An investigation of self-assembled polar InGaN quantum dots (QDs) on c-plane sapphire substrates by metal-organic chemical vapor deposition (MOCVD) is reported. The radiative exciton lifetime is measured by time-resolved photoluminescence at a low temperature of 18 K, where the non-radiative recombination can be negligible. A mono-exponential exciton decay with a radiative exciton lifetime of 707 ps for the capped QDs is preserved. The short radiative lifetime of 480 ps for uncapped QDs is revealed. With an optimized GaN capping layer grown by a two-step method, a radiative exciton lifetime of 707 ps for the capped QDs is preserved. The short radiative exciton lifetime is much shorter than that for previously studied polar QDs and is even comparable with those grown along non-polar QDs, which is strong evidence of the reduction of built-in fields in these polar InGaN QDs.

1. Introduction

Group-III-nitride-based quantum dots (QDs) are an excellent active material for optoelectronic devices such as light emitting diodes (LEDs), laser diodes and quantum light sources [1–7]. It is well known that the density of states becomes a delta function when there is three-dimensional confinement of carriers in QDs with a size below the exciton Bohr radius [8]. However, in comparison to the Bohr radius of larger than 10 nm in traditional InGaAs QDs [9], a Bohr radius of only around 3 nm makes it difficult for InGaN to realize ideal QDs [10]. The majority of studies on disk-shaped InGaN QDs of several tens of nanometers in width and of a small height lower than the Bohr radius are realized with quasi three-dimensional confinement. InGaN QDs with a lateral size of 25 nm and 40 nm fabricated by site-controlled and catalyst-free growth of the dot-in-wire method have been reported for use in a single photon source [11]. Self-organization is also more likely to form truncated pyramidal/disk-shaped QDs, and a base width in the range of 20–100 nm has been grown in the Stranski-Krastanov (SK) mode [12, 13].

InGaN QDs grown by molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) have shown the potential of the SK growth mode in achieving high-density dislocation-free InGaN QDs [12, 14–16]. However, a large built-in field across c-plane-strained InGaN QDs results in the spatial separation of the electron and hole wavefunctions. The quantum confined Stark effect (QCSE) leads these QDs to suffer from long exciton lifetimes [1]. For c-plane InGaN QDs, which typically have an extremely long radiative lifetime in the order of nanoseconds (ns) [17], only the dot-in-wire system has been reported to give a radiative lifetime in the order of a few hundred picoseconds (ps) [18]. To the best of our knowledge, the lowest reported radiative lifetime for c-plane InGaN QDs grown on GaN substrates by MBE is only 1.5 ns and on GaN/sapphire pseudo-substrate by MOCVD is 1–1 ns [19, 20].

In this letter, we present self-assembled polar InGaN QDs with short exciton lifetimes grown by MOCVD. A GaN capping layer was grown using a two-step method of low- and high-temperature growth to reduce non-radiative recombination pathways at the surface and to improve the uniformity of the QDs. Room-temperature photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements were carried out to investigate the optical properties and carrier recombination processes of the QDs.

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2. Experimental details

The InGaN QD samples were grown in a 6 × 2 inch AIXTRON Close Coupled Showerhead (CCS) MOCVD reactor equipped with an in situ monitoring system (LayTec EpiTT). The growth procedure is schematically summarized in figure 1, with the growth temperature plotted against time. Thermal cleaning was initially performed to remove the contaminants at the surface of the c-plane sapphire substrate. This was followed by growth of a GaN nucleation layer, an undoped GaN layer and a 3.5 μm silicon-doped n-GaN layer with electron concentration of 1 × 10^{18} cm^{-3} to form a GaN template for QD growth. The InGaN QDs and GaN capping layer employ triethylgallium, trimethylindium and ammonia as precursors and nitrogen as a carrier gas. Three separate growth runs of QDs, each with varied parameters of the capping layer, were carried out on the GaN-on-sapphire template. Sample A included an uncapped layer of InGaN QDs grown at 670 °C with a V/III ratio of 1.02 × 10^{4}. The Indium composition of InGaN QDs is around 22%. Samples B and C with a capping layer were used for future LED devices. For sample B, a 2 nm low-temperature GaN capping layer (LT-cap) was grown at the same temperature as the QDs. For sample C, the GaN capping layer was grown using a two-step method, a series of low- and high-temperature growth. The growth conditions, including the growth time and growth temperature of the LT-cap, were exactly the same as for sample B. The growth time of the high-temperature capping layer (HT-cap) for sample C is 400 s. It should be noted that the capping layer is typically grown at relatively low temperatures to prevent a decrease of the indium content or even a complete dissolution of the QDs. The growth temperature of the HT-cap for sample C is 830 °C, and the HT-cap thickness of sample C was estimated to be around 16 nm.

Atomic force microscopy (AFM) was performed using a Dimension 3100 atomic force microscope in tapping mode. Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) was used to analyze the concentration and location of elemental indium. Photoluminescence (PL) spectra of the samples were measured at room temperature using a 30 mW HeCd laser operating at 325 nm focused to a diameter of about 500 μm. Time-resolved photoluminescence (TRPL) measurements were performed at room temperature (300 K) and 18 K using a Hamamatsu streak camera (temporal resolution: 2 ps) and a femtosecond pulsed laser (wavelength: 266 nm, repetition rate: 76 MHz, pulse width: 200 fs) as the excitation source.

3. Results and discussions

The surface morphology of the GaN-on-sapphire template and sample A was characterized using an atomic force microscope over a 5 × 5 μm² scan region, as shown in figures 2(a) and (b). The corresponding root-mean-square (RMS) roughness value was found to be 0.3 nm for the GaN template, which provides a smooth surface for QD growth. The AFM measurements reveal uniformly distributed QDs along with clear GaN step flow patterns. The surface density and the average diameter of the QDs are approximately 1 × 10^{10} cm^{-2} and 66 nm, respectively. The height histogram of the QDs is extracted from the AFM data, as shown in figure 2(c). The unimodal Gaussian fitting shown by the dashed curve in figure 2(c) suggests good QD uniformity for sample A. The height distribution is centered at 2.5 nm with a full width at half maximum (FWHM) of 0.88 nm for sample...
A. Figure 2(d) shows the 5 × 5 μm² AFM image of sample B with the LT-cap. The GaN steps can still be observed to have a similar nanostructure distribution, and the RMS roughness for this sample is 0.5 nm, which is comparable to sample A. The uniform coverage is mainly attributed to the LT-cap being grown at the same growth temperature as the QDs, which prevented the dissolution of the QDs. This in turn led to a smoother surface morphology, which is important for the future multilayer growth of QDs.

Transmission electron microscopy (TEM) observations were performed on a JEOL JEM-2010F electron microscope operating at 200 kV. Figure 2(e) is a TEM image of sample C taken along the GaN [110] direction. The total thickness of the LT-cap and HT-cap are determined to be 18 nm. The height and diameters of the typical truncated pyramidal QDs are 2.3 nm and range from 60–85 nm, respectively, which is consistent with the AFM measurement results. The height of these QDs is lower than the exciton Bohr radius. Therefore, the quantum confinement in the (0001) direction is strong enough for the localization of excitons. Even though the quantum confinement is neglected along the lateral direction, the quantum confinement in that direction renders the optical properties significantly different from those of continuous quantum wells. It should be noted that the isolation space between QDs can enhance the lateral localization of carriers expected in defect-free QDs. In addition, it can impede the lateral diffusion of carriers to nonradiative recombination centers and improve the radiative efficiency [21].

The SIMS depth profiles of sample A, B and C are shown in figure 3(a). The indium peaks correspond to the InGaN QDs’ positions. Given the thickness of the capping layers, the indium peak of sample A is located at the surface, followed closely by the indium peak of sample B. A steady increase of indium intensity with increasing depth can be observed in sample C. The total capping layer thickness of 18 nm is consistent with the above TEM results. Figure 3(b) illustrates the SIMS depth profiles of sample C for the elements indium, gallium and oxygen. The depth profiles of gallium and oxygen are higher at the surface but soon decay to a constant value. An obvious valley for these two elements is observed precisely at the indium peak position. The drop in the gallium intensity is expected because of the formation of InGaN QDs. Oxygen from O-related defects reacting with gallium to form Ga2O3 and the subsequent evaporation away from the wafer surface during growth results in a drop in the oxygen intensity [22, 23]. This consequently reduces O-related defects and improves the crystalline quality. This observation is consistent with the nature of InGaN QDs, which inherently contain a lower density of structural defects [1, 24], and the improvement in crystalline quality during the QD formation [25].

In order to understand the PL properties of the QDs influenced by the capping layers, the optical properties of the three QD samples were investigated by PL measurement at room temperature (300 K). The PL spectra of these QD samples are shown in figure 4(a). The low energy emission (∼550 nm) is due to the yellow-band emission, which is a common phenomenon of GaN material grown by different methods with different growth conditions [26]. Therefore, the PL intensity of this low energy emission is less sensitive to the capping layer. It has been reported that the inhomogeneous size distribution and variation of the indium composition results in a broadened PL spectrum with a FWHM larger than 70 nm [27, 28]. The PL peak wavelength of sample A, located...
at 493 nm with a FWHM of 37 nm, suggests good uniformity of the QDs. Using the LT-cap, an approximately 20% PL intensity enhancement and a FWHM reduction to ∼31 nm can be observed in sample B in figure 4(b). The peak position of sample B is blueshifted by 3 nm compared to sample A. These results reveal that the LT-cap can effectively protect the InGaN QD layer from indium desorption.

Adding the HT-cap for sample C, the PL intensity increases at least two-fold, with a FWHM of 34 nm. The peak position of sample C is redshifted by 2 nm compared to sample A. The increase in PL intensity with the HT-cap most likely stems from increased absorption by the GaN capping layer, which feeds more carriers into the QDs. Another possible reason is that ramping of the temperature from the LT-cap to HT-cap growth acts as an annealing process, which reduces the non-radiative recombination at interface defects after the coverage of the LT-cap. This results in an enhancement of the PL quantum yield and narrowing of the emission peak. The pronounced redshift with the HT-cap is attributed to not only the QCSE but also the high-temperature annealing process, which can alter the shape, the strain, and the indium composition of the QDs. The increase in luminescence efficiency with the addition of the HT-cap indicates the beneficial role of the appropriate high-temperature process.

TRPL was used to investigate the carrier dynamics of the QDs and the internal built-in fields effect. Figure 5(a) displays the TRPL spectrum from all three samples at room temperature. The temporal behavior of the luminescence exhibits a mono-exponential process. Typically, there are two decay stages with a biexponential function due to the fluctuation of c-plane QDs in size and indium composition. In addition, both decay lifetimes are larger than a nanosecond [16, 29]. Therefore, the mono-exponential decay indicates the uniformity of the QDs, which is consistent with the Gaussian height distribution revealed by AFM measurements.
The TRPL results reveal that the recombination lifetime for excitons of the uncapped QDs increases from 130 to 307 ps after the addition of the LT-cap. A GaN capping layer grown at the low temperature of 670 °C by MOCVD has been reported to be associated with poor crystalline quality due to the limited adatom mobility on the growth surface [30]. The lifetime increase is, therefore, presumably a result of the poor crystalline quality of the low-temperature GaN growth. The crystalline quality of the LT-cap and the QDs are both improved through high-temperature annealing. Consequently, the lifetime is reduced from 307 to 160 ps for sample C with the HT-cap. However, the influence of annealing at high temperature is more complicated since there is also a change in the shape, size and indium composition of the QDs. The high-temperature capping layer may enhance column-III vacancy-related and impurity-enhanced diffusion, which leads to a longer lifetime [31, 32]. Secondly, the exciton lifetime strongly depends on the size of the QDs [33, 34]. Sample C having a comparable lifetime to sample A indicates that there are no obvious changes in the size of the QDs. In addition, considering that this recombination lifetime for the excitons are dominated by the non-radiative recombination. These comparable lifetimes mean the HT-cap growth leads to a reduction of the non-radiative recombination induced by the LT-cap growth.

Figure 4 (b) shows the mono-exponential decay spectrum test at 18 K for samples A and C with a radiative lifetime of 480 and 707 ps, respectively, and the internal quantum efficiency (IQE) is calculated to be 27% and 23%, respectively, assuming that the non-radiative recombination is completely eliminated at 18 K. The IQE of sample C lower than sample B is because sample C has low quality LT-cap layer. Sample B shows the radiative lifetime is 1.4 ns, which is due to the low quality of LT-cap layer. The radiative lifetime of sample C, with a thick GaN capping layer, is larger than that of sample A, consistent with an increasing built-in field, which results in a redshift via the QCSE. Figure 4(c) shows the variation of recombination lifetime with temperature for samples A, B and C. The lifetime decreases with increasing temperature, indicating the dominance of the non-radiative recombination. In the range of 50 K to 150 K, the lifetime of sample A increases with increasing temperature. The lifetime of sample B increase with increasing temperature from 18 K to 50 K. This is because the recombination
occurred in localized states other than free states [29, 35]. In contrast, for sample C, no localized states are observed, indicating the high-temperature capping layer improves the crystalline quality and uniformity of the QDs. Figure 5(d) shows the temperature-dependent PL extracted from TRPL of sample C. It is found that the PL intensity increased as the temperature decrease from 300 K to 18 K. Finally, from the literature, the reported recombination radiative lifetimes in various polar and non-polar InGaN QDs grown by MBE or MOCVD [17, 19, 36–39] are shown in figure 5(e), together with our data for the polar InGaN QDs. InGaN QDs grown on Si substrate [17], InGaN QDs incorporated in a laser structure [19] and InGaN QDs grown by a modified droplet epitaxy were compared [36–39]. Ours is the shortest radiative lifetime for InGaN QD growth along the c-plane, and is even comparable with QDs grown along non-polar orientations [38]. Figure 5(f) shows the band profile of a GaN/InGaN QD structure with and without built-in fields.

Figure 5. (a) Time-resolved PL for samples A, B and C at room temperature; (b) time-resolved PL for the sample A, B and C tests at 18 K; (c) temperature dependence of recombination lifetime for sample A, B and C; (d) the temperature-dependent PL extracted from TRPL of sample C; (e) the reported and our data of recombination radiative lifetime; and (f) the band profile of a GaN/InGaN QD structure with and without built-in fields.
proportional to the overlap of electron and hole wave-functions [40], this shorter lifetime suggests an even stronger overlap and reduction of the polarization fields.

4. Conclusions

In conclusion, self-organized polar InGaN QD samples were grown on GaN-on-sapphire templates by MOCVD. The optical properties of the InGaN QDs with a two-step growth of the capping layer were investigated. The PL emission intensity was enhanced following the addition of this two-step growth, with a smaller FWHM of 34 nm. The mono-exponential decay process of the TRPL spectrum was consistent with the height distribution in the unimodal Gaussian function, implying the uniformity of the QDs. A significantly shorter lifetime was observed in the c-plane QDs due to the increased overlap of the electron and hole wave-functions. These results indicate that it is possible to minimize the built-in fields for c-plane InGaN QDs.

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