Long-time evolution of the photoluminescence in *C*- and *M*-plane GaN/AlN quantum dots upon intense ultraviolet irradiation

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We compare the spontaneous emission of *C*- and *M*-plane GaN quantum dots embedded in AlN. *C*-plane dots are characterized by an intense emission with an exceptionally long decay time up to room temperature. In contrast, *M*-plane dots exhibit a much weaker emission with a very short decay time. In addition, the emission of the *C*-plane dots temporally evolves on a timescale of seconds, while the emission of the *M*-plane dots is stable over time. These findings are correlated with the different growth mode and microstructure of *C*- and *M*-plane GaN quantum dots. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2973404]

Among the most unexpected and fascinating phenomena in the research of quantum dots (QDs) is the long-time (millisecond to second) dynamic behavior of their spontaneous emission. The spectral jitter and the random-telegraph intensity variations ("blinking") of individual transitions are the most prominent examples for these phenomena, which were originally observed for colloidal QDs and are commonly attributed to the presence of slow traps.[1–3] More recently, related processes have also been observed for epitaxial QDs.[4–7] Here, we present experimental results for epitaxial, differently oriented wide-gap GaN/AlN QDs. We believe that the observed temporal changes also belong to this class of trap-induced effects.

C- and *M*-plane GaN/AlN QDs are grown on $6H$-SiC(0001) and $6H$-SiC($1\bar{1}00$) substrates, respectively, by plasma-assisted molecular beam epitaxy (MBE). Substrate preparation and growth of the 100 nm thick AlN buffer layer are described in detail in Ref. 8. Note that a polytype replication occurs on $6H$-SiC($1\bar{1}00$), i.e., the *M*-plane structure predominantly exhibits a $6H$ stacking sequence. The *C*-plane (*M*-plane) sample MQD-C (MQD-M) consists of ten GaN QD layers separated by 10 nm AlN, while the corresponding sample SQD-C (SQD-M) contains a single QD layer capped with 30 nm AlN. To initiate QD growth, 1 nm GaN is deposited under Ga-stable conditions. For the *C*-plane samples, QDs form upon a growth interruption via strain-induced ripening,[9,10] while Volmer–Weber growth occurs in the case of the *M*-plane samples. Atomic force microscopy (not shown here) reveals a high density of QDs (10^{11} cm^{-2}) with an average height of 2.5 nm for MQD-C and 2 nm for MQD-M. The QDs are irregularly shaped in the case of MQD-C, but strictly rectangular for MQD-M. In both cases, the lateral size distribution (15 ± 10 nm) is very wide.

The samples are studied by cathodo- (CL) and photoluminescence (PL) spectroscopy. The CL investigations are performed at 5 K in a Carl Zeiss ULTRA 55™ scanning electron microscope equipped with an Oxford mono-CL3™ and a He-cooling stage. A 0.3 m monochromator and a cooled photomultiplier is used in conjunction with conventional photon-counting techniques to disperse and detect the CL signal, respectively. Continuous-wave (cw) PL measurements are carried out using a Cryovac microscope cryostat. For excitation, we use the 325 nm line of a Kimmon He–Cd laser focused to a micrometer-sized spot by a 40× microscope objective. The PL signal is collected by the same objective and analyzed by a 0.8 m Jobin-Yvon monochromator equipped with a cooled charge-coupled-device detector. The PL decay time is measured with the samples mounted in a He-flow cryostat allowing continuous temperature control between 4 and 300 K. A Coherent Mira™ femtosecond Ti:sapphire laser is used for excitation. The 200 fs laser pulses with a repetition rate of 76 MHz are frequency tripled and tuned to an excitation wavelength of 230 nm, resonant to the transition energy of a single monolayer (ML) thick GaN quantum well in AlN (see below).[11] The luminescence is dispersed by a 0.22 m monochromator and focused onto the photocathode of a Hamamatsu streak camera. The overall time resolution of this setup is better than 5 ps.

An important experimental issue when dealing with the exposure of semiconductor surfaces to intense ultraviolet lasers *in vacuo* is the rapid buildup of cracked hydrocarbons, ultimately forming an amorphous opaque residue. This contamination is essentially inevitable for semiconductors stored in air even when thoroughly cleaned, but may not be noticed for weak excitation and short measurement times. For the present conditions, however, contamination is a serious problem since the incident intensity is on the order of several kW/cm^2 and the exposure duration amounts to several minutes. We have found that an *in situ* ozone cleaning in the optical cryostat provides a convenient and effective solution to this problem. Provided that the cryostat is equipped with windows transparent down to 184.9 nm (such as permitted by windows consisting of synthetic fused silica), a 10 W low-pressure Hg discharge lamp placed just in front of the window will suffice to effectively remove all hydrocarbons from the surface of samples mounted close to the window (preferably less than 1 cm distance).[12] After this step, the cryostat should be evacuated to a pressure $<10^{-5}$ mbar prior to cooling. Following this procedure, we found the PL signal from thick GaN films to be stable under continuous exposure to the laser for time spans of at least 1 h.

Figure 1 shows the CL spectra of samples MQD-C and MQD-M. The spectra are dominated by a broad band centered at 340 and 310 nm for MQD-C and MQD-M, respec-

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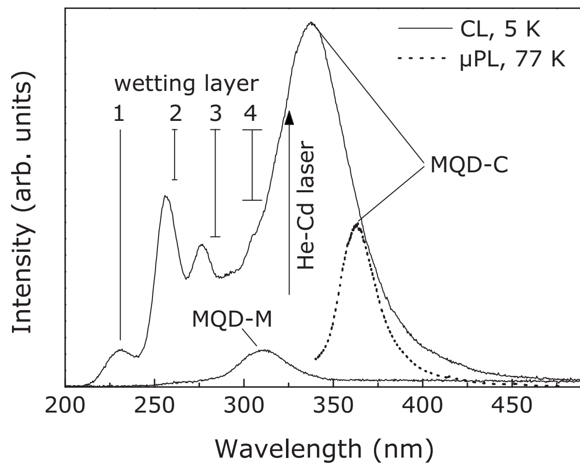

FIG. 1. CL spectra of samples MQD-C and MQD-M (solid lines) measured at 5 K. The vertical lines indicate the emission energy calculated for a 1–4 ML thick GaN/AlN quantum well (the wetting layer). The horizontal bars denote the range obtained with and without taking into account the internal electrostatic field. The arrow indicates the He–Cd laser line used to obtain the PL spectrum of MQD-C at 77 K (dotted line).

tively. The integrated CL intensity for the former sample is more than one order of magnitude higher compared to that of the latter. Furthermore, MQD-C exhibits three high-energy transitions, the spectral positions of which basically agree with the calculated ones for a wetting layer of 1–3 ML in thickness.[13] These transitions are absent for MQD-M, reflecting the different growth modes on the *C*- and *M*-planes. Note that the spectral position of the QD transitions depends in a complex way on the size, shape, and strain of the QDs.[14]

Figure 1 also shows the spectral position of the He–Cd laser line used to excite cw-PL. Evidently, neither the AlN barrier nor the GaN wetting layer can be excited at this wavelength (325 nm), but for MQD-C, the QDs are excited resonantly. This resonant excitation results in a highly selective excitation of a certain class of QDs since excitons can only be generated in QDs with an excited state at or close to the excitation wavelength. This fact, consequently, results in a redshift of the PL spectrum (dotted line in Fig. 1) compared to the CL spectrum of MQD-C. For MQD-M, the He–Cd laser line coincides with the low-energy side of the QD emission and apparently cannot excite the QDs at all since no signal is detected apart from the substrate luminescence.

Upon pulsed excitation at 230 nm, a weak signal is detected from MQD-M at 380 nm. However, the decay time of this PL band is too short to be measured (<5 ps). This finding is identical to the one obtained for thick GaN films fabricated using the same N_2 plasma source, which is known for producing high-energy ions resulting in significant ion damage and thus very short nonradiative lifetimes. In complete contrast, these time-resolved PL measurements reveal a constant decay time of 1 ns between 10 and 300 K for MQD-C. This exceptionally long decay time for a sample grown under exactly the same conditions as MQD-M can be understood by the particular formation mechanism of these *C*-plane QDs, namely, the ripening: point defects created during growth by high-energy N^+ ions are effectively removed by the inevitable mass transport initiated by the strain-induced ripening observed for the *C*-plane samples such as MQD-C. Ripening reorders the crystal, and thus acts similarly to a high-temperature annealing for the material involved.

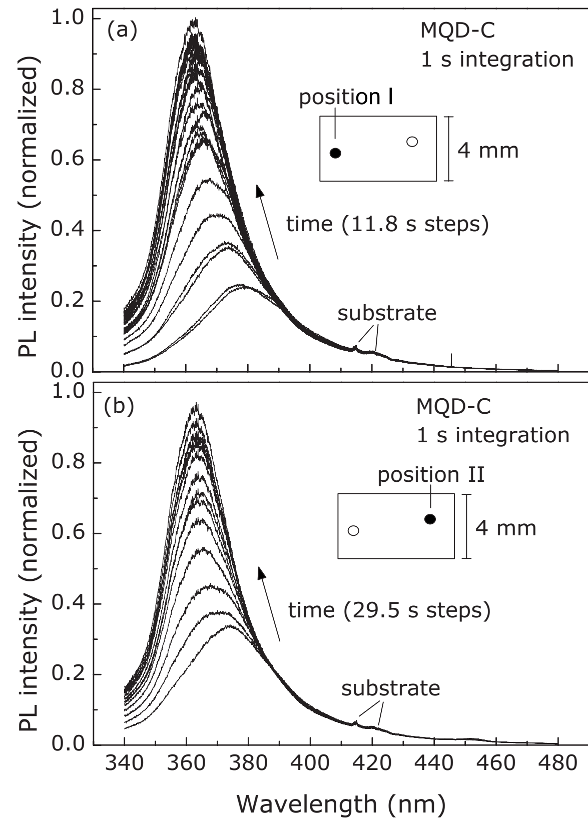

FIG. 2. Temporal evolution of the PL spectrum of sample MQD-C for (a) position I and (b) position II on the sample as indicated. The spectra are obtained at 77 K with an excitation density of 20 kW/cm^2.

When excited by the 325 nm line of the He–Cd laser, the broad PL band of sample MQD-C hardly varies its spectral position and intensity between 10 and 300 K. However, at temperatures around 77 K, an interesting phenomenon is observed, as displayed in Figs. 2(a) and 2(b). At the highest excitation density of 20 kW/cm^2, the PL band changes with increasing exposure time. Specifically, the band spectrally blueshifts, narrows its width, and gains intensity. This observation is reproducible across the whole sample as demonstrated by the comparison between Figs. 2(a) and 2(b). These spectral changes become unmeasurably slow at temperatures below 50 and too fast to record at temperatures above 100 K.

Figures 3(a)–3(c) display the temporal evolution of the spectral position, full width at half maximum, and intensity of the QD emission band, respectively. The spectral blueshift amounts to 25 nm (0.2 eV), the linewidth is reduced from 40 to 25 nm (0.32–0.2 eV), and the integrated intensity increases by a factor of 2. All of these changes occur simultaneously and hence must have a common origin. Indeed, a consistent explanation of this phenomenon is provided when assuming that slow traps, which capture one sort of carriers, exist within the QD (since excitons are created resonantly directly in the QD). The capture of, e.g., holes by these traps would cause a charging of the QDs, and the remaining electrons would screen the electrostatic field within the QD. Naturally, a screening of this field would counteract the quantum confined Stark effect and would thus result in a blueshift, a narrowing, and an enhancement of the intensity of the emission. Note that the calculated strength of the internal field in the QD is as high as 6–9 MV/cm,[15,16] and even a partial screening of this field is more than sufficient to account for the changes observed.[15]

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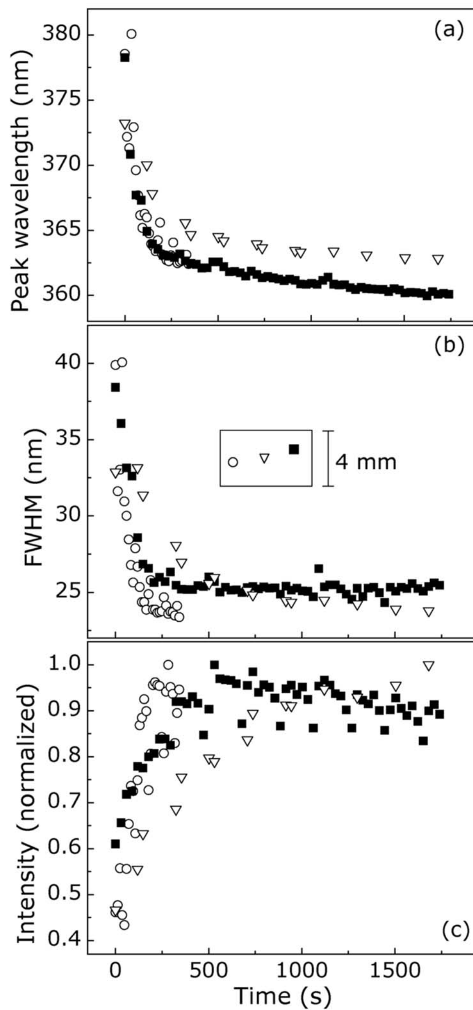

FIG. 3. (a) Peak wavelength, (b) full width at half maximum, and (c) integrated intensity of the emission from MQD-C at three different sample positions as schematically shown in the inset in (b).

When accepting this hypothesis, the origin of these traps is of course an immediate question. Figures 4(a) and 4(b) show a comparison between samples SQD-C and SQD-M, respectively. The evolution of the PL spectra for the former sample is similar to that observed above, while the small intensity variation observed for the latter is random. In fact, *all* of the *C*-plane samples we have investigated (also one grown by reactive MBE, a growth technique which is inherently free of ion damage) exhibit a similar temporal evolution of the PL spectra as shown exemplary in Fig. 2, while *none* of the *M*-plane samples do. A likely candidate for the origin of our hypothetical traps is the different microstructure of *C*- and *M*-plane films. The defect structure of *C*-plane AlN films is dominated by perfect edge dislocations with a typical density of several 10^{10} cm^{-2} and above.[17] In contrast, we hardly find any perfect dislocations in *M*-plane AlN films, whose defect structure is characterized by stacking faults (and associated partial dislocations) with a density of typically 10^5 cm^{-1}.

In conclusion, the above trap hypothesis explains the slow changes of the PL spectra in *C*-plane QDs in a simple way. Concerning the origin of these slow traps, we speculate that they might originate from threading dislocations which intersect *C*-plane samples in abundance (approaching or even exceeding 10^{11} cm^2) but are virtually absent in *M*-plane

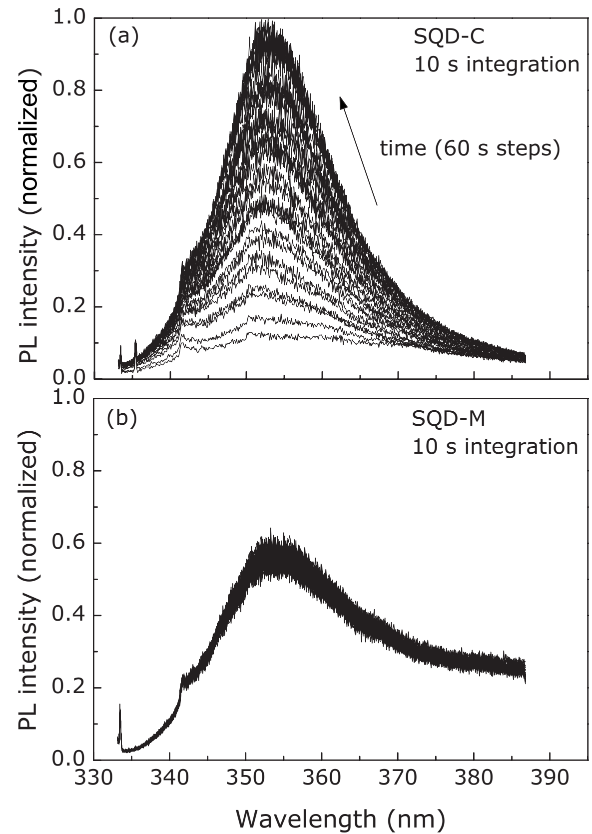

FIG. 4. Temporal evolution of the PL spectra of (a) SQD-C and (b) SQD-M. The spectra are obtained at 77 K with an excitation density of 20 kW/cm^2.

samples. Since it has been observed that GaN QDs nucleate preferentially next to edge threading dislocations propagating through AlN,[17] it is indeed possible that excitons resonantly generated within the GaN QD interact with these dislocation-induced traps as suggested by our results.

[1]A. L. Efros and M. Rosen, Phys. Rev. Lett. **78**, 1110 (1997).
[2]P. A. Frantsuzov, Phys. Rev. B **72**, 155321 (2005).
[3]J. Tang and R. A. Marcus, J. Chem. Phys. **123**, 054704 (2005).
[4]D. Bertram, M. Hanna, and A. Nozik, Appl. Phys. Lett. **74**, 2666 (1999).
[5]C. Santori, D. Fattal, J. Vučković, G. Solomon, E. Waks, and Y. Yamamoto, Phys. Rev. B **69**, 205324 (2004).
[6]R. Micheletto, M. Abiko, A. Kaneta, Y. Kawakami, Y. Narukawa, and T. Mukai, Appl. Phys. Lett. **88**, 061118 (2006).
[7]R. Bardoux, T. Guillet, P. Lefebvre, T. Taliercio, T. Bretagnon, S. Rousset, B. Gil, and F. Semond, Phys. Rev. B **74**, 195319 (2006).
[8]D. M. Schaadt, O. Brandt, A. Trampert, H.-P. Schönherr, and K. H. Ploog, J. Cryst. Growth **300**, 127 (2007).
[9]C. Adelmann, N. Gogneau, E. Sarigiannidou, J.-L. Rouvière, and B. Daudin, Appl. Phys. Lett. **81**, 3064 (2002).
[10]J. S. Brown, P. M. Petroff, F. Wu, and J. Speck, Appl. Phys. Lett. **84**, 690 (2004).
[11]Due to the fact that a wetting layer is present on the (0001) but absent on the $(1\bar{1}00)$ plane, the carrier density generated by the 230 nm pulse is presumably higher for the *C*-plane samples than for their *M*-plane counterparts.
[12]J. R. Vig, J. Vac. Sci. Technol. A **3**, 1027 (1985).
[13]J. S. Brown, P. M. Petroff, F. Wu, and J. Speck, Jpn. J. Appl. Phys., Part 2 **45**, L669 (2006).
[14]A. D. Andreev and E. P. O'Reilly, Phys. Rev. B **62**, 15851 (2000).
[15]V. Ranjan, G. Allan, C. Priester, and C. Delerue, Phys. Rev. B **68**, 115305 (2003).
[16]T. Bretagnon, P. Lefebvre, P. Valvin, R. Bardoux, T. Guillet, T. Taliercio, B. Gil, N. Grandjean, F. Semond, B. Damilano, A. Dussaigne, and J. Massies, Phys. Rev. B **73**, 113304 (2006).
[17]J. L. Rouvière, J. Simon, N. Pelekanos, B. Daudin, and G. Feuillet, Appl. Phys. Lett. **75**, 2632 (1999).

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