PHYSICAL REVIEW B VOLUME 57, NUMBER 16 15 APRIL 1998-II

Reduction of oscillator strength due to piezoelectric fields in $GaN/Al_xGa_{1-x}N$ quantum wells

Jin Seo Im,* H. Kollmer, J. Off, A. Sohmer, F. Scholz, and A. Hangleiter
4. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, D-70550 Stuttgart, Germany

(Received 15 December 1997)

We demonstrate a dramatic reduction of the oscillator strength in $GaN/Al_xGa_{1-x}N$ quantum wells due to piezoelectric fields. Our study using time-resolved photoluminescence spectroscopy reveals a strong increase of the luminescence decay time of the dominating transition with increasing well width by several orders of magnitude in parallel to a redshift of the emission peaks. The experimental results are consistently explained by a quantitative model based on the piezoelectric fields in strained wurtzite quantum wells. We estimate the piezoelectric constant of GaN to $d_{31} = -0.9\times10^{-10}$ cm/V. [S0163-1829(98)52016-4]

GaN-based quantum wells (QW's) have been successfully applied in blue and green light emitting laser diodes as well as in violet laser diodes.[1,2] Despite the poor material quality of epitaxial nitride layers compared to other III-V semiconductors, those devices have shown high performance and high reliability.

In parallel to the progress in the fabrication of optical devices, there have been lively discussions about the optical properties of quantum wells based on GaN, $Al_xGa_{1-x}N$, and $Ga_{1-x}In_xN$. Particularly for $Ga_{1-x}In_xN/GaN$ QW's, it has been noted for some time that there exists a large redshift of the optical emission spectrum as compared to the absorption. Together with other features, such as an energy-dependent decay time of the emission in quantum wells, this has often been interpreted in terms of localization of excitons at composition fluctuations or even the formation of quantum dots due to local phase separation of InN and GaN.[3,4]

Recently, it has been proposed that piezoelectric fields due to mismatch-induced strain in $Ga_{1-x}In_xN/GaN$ QW's are the primary reason for the large redshift of the luminescence.[5] In fact, the strongly polar Ga-N bond should give rise to rather large piezoelectric charges in the wurtzite structure when subject to elastic strain. On the other hand, in the presence of the piezoelectric field, the electron and hole wave functions separate spatially leading to a reduced overlap and hence a reduced recombination rate. To the best of our knowledge, there has been no report on the recombination rate influenced by piezoelectric fields in GaN-based materials until now.

$GaN/Al_xGa_{1-x}N$ QW's are well suited to investigate the optical properties of the GaN-based QW, because effects like composition fluctuations are not expected. Therefore, in this paper, we have studied $GaN/Al_xGa_{1-x}N$ QW's using time-resolved photoluminescence (TRPL) spectroscopy. Our study exhibited a dramatic decrease in oscillator strength by several orders of magnitude with increasing well thickness, which can only be explained by large piezoelectric fields up to 1 MV/cm.

Our samples were grown on (0001)-oriented sapphire substrates using low-pressure metalorganic vapor phase epitaxy. A nucleation layer of about 10 nm AlN grown at 800 °C was employed improving the quality of the upper nitride layers grown at 1000 °C. The layers consist of a nominally undoped GaN double heterostructure that is sandwiched between a 500 nm $Al_xGa_{1-x}N$ buffer and a 50 nm $Al_xGa_{1-x}N$ cap layer. The AlN mole fraction of barrier layers was estimated as 0.15 from photoluminescence spectra. The thickness of the GaN layers was varied between 1.3 nm and 100 nm. In the measurements, the samples were resonantly excited with 5 ps pulses from a frequency-doubled, cavity-dumped dye laser (Pyridine 1), which was pumped by a mode-locked Nd:yttrium aluminum garnet laser. The wavelength is tunable between 337 nm and 376 nm, and the repetition rate was selected between 4 MHz and 8 kHz depending on the decay time in order to avoid multiexcitation. The luminescence is dispersed by a 0.75 m grating monochromator, detected by a Hamamatsu R3809 microchannel-plate photomultiplier, and processed using time-correlated, single-photon-counting electronics. An appropriate deconvolution technique provides a time resolution of 15 ps. All measurements (time-resolved and time-integrated photoluminescence spectroscopy) were done at 5 K.

Time-integrated low-temperature luminescence spectra of $GaN/Al_xGa_{1-x}N$ QW's under resonant excitation are shown in Fig. 1. The 100 nm double heterostructure (DH) reveals a spectrum similar to that of bulk GaN, due to the fact that quantum confinement effects are negligible. The emission of excitons at about 3.5 eV dominates the spectrum of the 100 nm DH, but the peak originating from donor-acceptor-pair

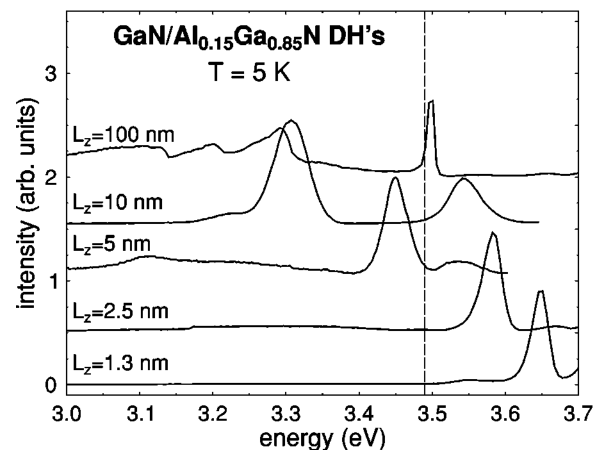

FIG. 1. Time-integrated photoluminescence spectra of a series of $GaN/Al_xGa_{1-x}N$ double heterostructures (DH's). The dashed line indicates the position of the GaN band gap.

 © 1998 The American Physical Society

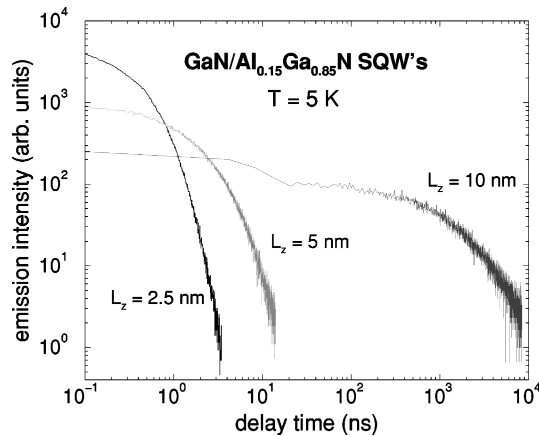

FIG. 2. Double-logarithmic plot of the luminescence decay for a 2.5 nm, a 5 nm, and a 10 nm GaN/$Al_xGa_{1-x}N$ single quantum well. The thickest layer shows a decay on a μs time scale.

recombination and its phonon replicas are also recognizable. On the other hand, the luminescence spectra of GaN/$Al_xGa_{1-x}N$ QW's exhibit a fairly complex behavior. We observe two emission lines from thick QW's but only a single line from thin QW's. Thin QW's (1 nm and 2 nm) show a clear blueshift of their emission due to size quantization. In thicker layers (5 nm and 10 nm), the higher-energy emission line lies about 70 meV above the GaN band gap, whereas the lower-energy line shifts to energies well below the GaN band gap with increasing thickness.

The luminescence decay time was measured at the emission peaks in the spectra, and the typical decay traces are depicted in Fig. 2. The single emission line in thin QW's (1.3 nm and 2.5 nm) as well as the higher-energy line in thicker QW's (5 nm and 10 nm) have decay times of 200–300 ps. In contrast, the lower-energy emission lines in thicker layers (5 nm and 10 nm) show a strongly nonexponential decay, and their decay time scale extends into the μs range. For the 10 nm QW, the decay time obtained at a long delay time after pulsed excitation reaches 3 μs.

The temporal behavior of the spectrum of the lower-energy line was studied by TRPL spectroscopy. Time-resolved spectra of the 10 nm QW, observed at various times, are shown in Fig. 3. The spectra were integrated at each time interval, and their intensity was normalized. The

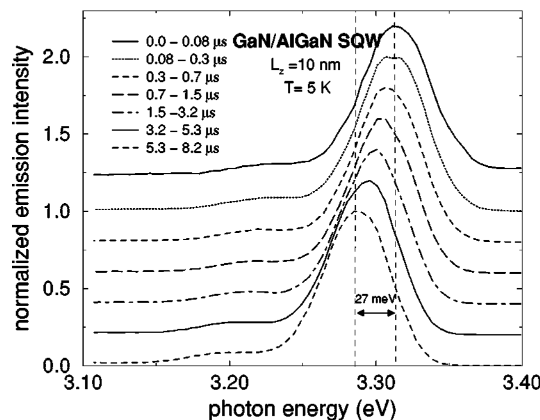

FIG. 3. Time-resolved spectra of the lower-energy line of a 10 nm GaN/$Al_xGa_{1-x}N$ single quantum well.

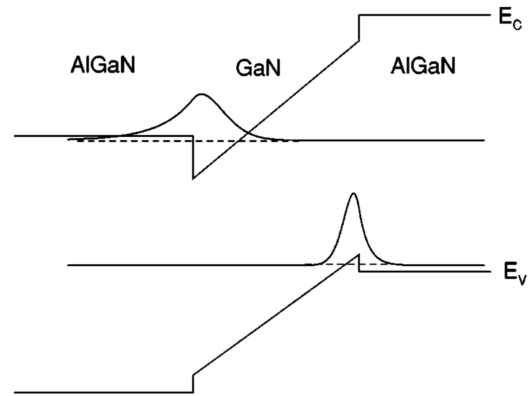

FIG. 4. Schematic picture of the energies and wave functions of electrons and holes in a strained quantum well with a piezoelectric field.

emission peaks in these spectra shift towards lower energy as time evolves. The redshift of the emission peak for a long delay time after pulsed excitation was obtained as 27 meV. The shape and linewidth of these spectra are not subject to change with increasing delay time.

In order to explain the origin of the emission peaks well below the GaN band gap, one might consider donor-acceptor-pair (DAP) recombination. The strongly nonexponential time decay and the redshift of the emission peaks with evolving time would comply with this model. But DAP transitions can be excluded since the peak energy and decay time is dependent on the well width. The emission peak below the GaN band gap in the 10 nm QW shifts to lower energy by about 150 meV as compared to the peak energy of the 5 nm QW, and the emission peak of the the 10 nm QW decays more slowly than that of the 5 nm QW. A DAP transition model cannot explain this behavior.

Another possible model would be localized states, e.g., due to fluctuations of the well width. This model is also confronted with a problem since such transitions could not be below the bulk GaN band gap. In addition, the localization energy of about 200 meV and a decay time on μs time scale would require a strong localization to a radius of less than 1 Å, which is clearly not feasible.

Let us now consider the consequences of piezoelectric fields. A qualitative picture is shown in Fig. 4. The $Al_xGa_{1-x}N$ barriers are assumed unstrained and have no piezoelectric field, while the GaN QW is under a biaxial compressive strain perpendicular to (0001), which induces a piezoelectric field. The broken line and solid curve in the valence and the conduction band indicate the energy level of the ground state and the wave function involved. Due to the piezoelectric field, energy levels of quantum wells shift towards lower energy with increasing well width. At the same time, the electron and hole ground-state wave functions are spatially separated leading to a dramatic reduction in oscillator strength. This behavior is in good agreement with our results from PL and TRPL spectra. For a quantitative calculation, we solved an effective-mass Schrödinger equation for the conduction and valence band using a spatially linearly varying potential energy in the quantum well. In this simple model, the quantization energy, the wave function, and the matrix elements were calculated at various well widths. The matrix elements are proportional to the square of the overlap

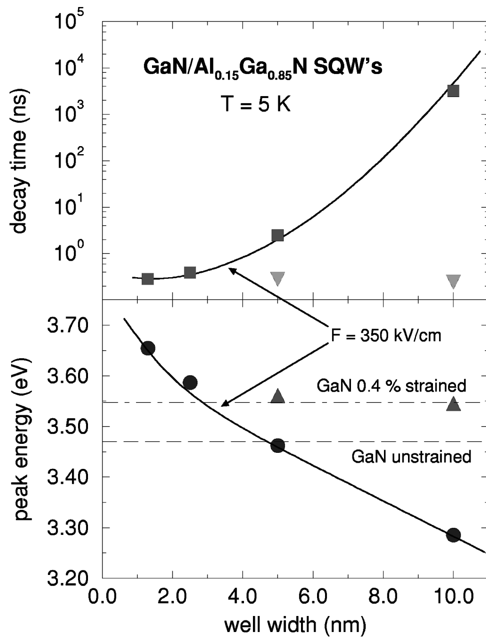

FIG. 5. Comparison of the measured energy positions (dots) and decay times (squares) of the low-energy lines in $GaN/Al_xGa_{1-x}N$ QW's with a calculation based on piezoelectric fields.

integral between electron and hole wave function. We used an effective electron mass of $0.2m_0$,[6] and a hole mass of $2.2m_0$,[7,8] assuming no difference between the effective masses of charge carriers in the QW and the barrier layers. The applied ratio between conduction and valence band discontinuity is 75:25.[9] A comparison of the calculated energies and oscillator strengths with the experimental data is shown in Fig. 5. For this figure, the energetic positions were taken from TRPL spectra at the longest possible delay time after excitation, i.e., with screening of the field being as small as possible. For the same reason, the decay time in the strongly nonexponential decay was also determined at a long delay time. The calculated curves include only a single adjustable parameter, which is the magnitude of the piezoelectric field. In the present case, a field of 350 kV/cm consistently explains both the redshift of the emission peaks and the dramatic increase of the decay time with increasing well width.

Moreover, Fig. 5 indicates that the higher-energy line in the thick layers is obviously associated with spatially direct transitions in the strained GaN well layer, since its transition energy coincides with the band gap of GaN under 0.4% compressive strain (dashed-dotted line). This is the strain expected for GaN embedded between $Al_{0.15}Ga_{0.85}N$ layers. Of course, these transitions can occur only directly after excitation. Optically excited carriers drift under the piezoelectric field, and they are being separated spatially with increasing time. The low mobility of carriers, particularly of holes, results in a large drift time leading to a long delay before establishing a spatial separation. During this process, the spatially direct transition could take place, especially at low temperatures where an extremely low mobility can be expected. On the other hand, excited carriers could be localized as excitons bound to donors or acceptors. The bound excitons would allow spatially direct transitions prior to a spatial separation due to the piezoelectric field.

It is interesting to use our data to estimate the piezoelectric constant of GaN. The piezoelectric field E_3 along the (0001) axis is expressed via the piezoelectric constant d_{31} as[10]

$$E_3=\frac{2\,d_{31}}{\epsilon_0\epsilon_r}\left(c_{11}+c_{12}-\frac{2\,c_{13}^2}{c_{33}}\right)\epsilon_{xx}, \tag{1}$$

where ϵ_0 and ϵ_r are the permittivity of the vacuum and the static dielectric constant of the material, respectively. ϵ_{xx} is the in-plain strain, and c_{ij} are the elastic constants. Recently, the GaN elastic constants have been determined by using a resonance ultrasound method as $c_{11}=377$ GPa, $c_{12}=160$ GPa, $c_{13}=114$ GPa, and $c_{33}=209$ GPa.[11] Using $\epsilon_r=9.5$,[12] we find $d_{31}=-0.9\times10^{-10}$ cm/V, which is somewhat smaller than the value of -1.7×10^{-10} cm/V estimated by Martin *et al.*[9]

Let us now discuss the consequences of our results on device operation. A strong piezoelectric field is also expected in strained $Ga_{1-x}In_xN$-based quantum wells. In this case, the energetic position of the emission is not only related to the In fraction in the active $Ga_{1-x}In_xN$ layer, but also to the piezoelectric field and the well thickness. Green light-emitting diodes (LED's) based on $Ga_{1-x}In_xN$, for instance, are likely to have a much lower In content than previously thought, with the piezoelectric shift being of the order 0.5 eV. On the other hand, the dramatic decrease of the oscillator strength with increasing strain and well thickness will also influence device performance. While for LED's, a long radiative lifetime may not be important within some limits, the small oscillator strength will definitely be detrimental for laser operation. This may in fact be the reason why it has proven to be difficult to extend the lasing wavelength of a nitride-based laser to beyond 440 nm.[13]

In conclusion, the effects of piezoelectric fields on the static and dynamic optical properties of $GaN/Al_xGa_{1-x}N$ single quantum wells were studied by time-resolved photoluminescence. We found a strong increase of the luminescence decay time of the dominating transition with increasing well thickness by several orders of magnitude in parallel to a redshift of the emission peaks. Our experimental findings are consistently explained by a quantitative model based on the piezoelectric fields in strained wurtzite quantum wells.

We would like to thank O. Gfrörer for helpful discussions. J.S.I. acknowledges support by the Deutscher Akademischer Austauschdienst. Financial support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

*Electronic address: j.s.im@physik.uni-stuttgart.de

[1] S. Nakamura, M. Senoh, S.-I. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto, and H. Kiyoku, Jpn. J. Appl. Phys., Part 2 **36**, L1059 (1997).

[2] S. Nakamura, M. Senoh, N. Iwasa, and S.-I. Nagahama, Appl. Phys. Lett. **67**, 1868 (1995).

[3] S. Chichibu, T. Azuhata, T. Sota, and S. Nakamura, Appl. Phys. Lett. **69**, 4188 (1996).

[4] Y. Narukawa, Y. Kawakami, M. Funato, S. Fujita, S. Fujita, and S. Nakamura, Appl. Phys. Lett. **70**, 981 (1997).
[5] T. Takeuchi, S. Sota, M. Katsuragawa, M. Komori, H. Takeuchi, H. Amano, and I. Akasaki, Jpn. J. Appl. Phys., Part 2 **36**, L382 (1997).
[6] B. K. Meyer, D. Volm, A. Graber, H. C. Alt, T. Detchprohm, H. Amano, and I. Akasaki, Solid State Commun. **95**, 597 (1995).
[7] J. S. Im, A. Moritz, F. Steuber, V. Härle, F. Scholz, and A. Hangleiter, Appl. Phys. Lett. **70**, 631 (1997).
[8] K. Kim, W. R. L. Lambrecht, B. Segall, and M. van Schilfgaarde, Phys. Rev. B **56**, 7363 (1997).
[9] G. Martin, A. Botchkarev, A. Rockett, and H. Morkoç, Appl. Phys. Lett. **68**, 2541 (1996).
[10] A. Bykhovski, B. Gelmont, and M. Shur, J. Appl. Phys. **74**, 6734 (1993).
[11] R. B. Schwarz, K. Khachaturyan, and E. R. Weber, Appl. Phys. Lett. **70**, 1122 (1997).
[12] J. W. Orton and C. T. Foxon, Rep. Prog. Phys. **61**, 1 (1998).
[13] S. Nakamura, IEEE J. Sel. Top. Quantum Electron. **3**, 435 (1997).