Time-resolved spectroscopy of strained GaN/AlN/6H-SiC heterostructures grown by metalorganic chemical vapor deposition

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Temperature-dependent time-resolved photoluminescence measurements were performed on GaN film/AlN buffer/6H-SiC substrate heterostructures grown by metalorganic chemical vapor deposition. The overlying GaN layers were under tension, as estimated from the free A exciton (FE_A) position. The recombination lifetimes were determined for the FE_A and for the neutral-donor-bound exciton (D_0X). We observed that the recombination lifetime for the FE_A has the same value of 40–50 ps in all the layers, whereas the recombination time for the D_0X varies for different samples. We observed that the recombination lifetimes for D_0X have a clear dependence on the position of FE_A , i.e., the recombination lifetime increases with decreasing strain in the layers. We discuss the results in term of the hole states involved in the donor-bound exciton recombination.

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GaN and related alloys are presently the most attractive materials for fabrication of optoelectronic devices in the ultraviolet and blue energy region.^{1,2} Due to the lack of suitable nitride substrate material, heteroepitaxial growth on sapphire or 6H-SiC substrates with AlN or AlGaIn buffer layers is common practice. The large lattice and thermal mismatches between GaN and these materials results in residual strain in the heterostructures that can be the source of serious problems (e.g., cracking and control over quantum well output) influencing the device quality. It also potentially affects device performance in ways that are not yet fully articulated. For instance, for device physics the carrier (or exciton) lifetime (τ) is a parameter of great importance; however it is still unclear how strain affects carrier lifetimes.

In order to investigate this issue, we performed time-resolved photoluminescence (PL) spectroscopy on strained wurtzite GaN epilayers of different thickness and correspondingly different strain states. We observed that the PL recombination time for the neutral donor-bound exciton (D_0X) varied depending on the samples and the value of the residual strain in the layers, whereas the recombination time for the free A exciton (FE_A) was practically the same in all of the samples investigated. We advance a preliminary explanation of these phenomena in terms of the hole states involved in the neutral donor-bound exciton recombination.

A set of GaN layers of comparable quality were grown with AlN buffer layers (1000 Å thick at 1000 °C) on 6H-SiC substrates by metalorganic chemical vapor deposition (MOCVD). All samples were undoped and grown with the same III-V flux ratio; the GaN layer thickness varied from 0.5 to 4.0 μm. Optical excitation was performed with a femtosecond pulse frequency-tripled beam of an Al₂O₃:Ti mode-locked laser (λ_{ex} = 266 nm). Photoluminescence (PL) was

detected by using a GaAs photomultiplier tube. The time-resolved measurements were performed using a syncroscan streak-camera system with a time resolution of about 20 ps.

The low temperature (2 K) PL spectra for the investigated GaN epilayers are shown in Fig. 1(a) by the solid lines; corresponding FE_A (open circles) and D_0X (open squares) energy positions are plotted versus in-plane residual stress in Fig. 1(b). The thickness of each GaN epilayer is indicated in Fig. 1(a). For comparison, we also show the PL spectrum taken for an 80-μm-thick GaN layer [dashed line in Fig. 1(a); solid square and circle in Fig. 1(b)] grown by hydride vapor-phase epitaxy (HVPE) on sapphire,³ since material grown on sapphire is typically under compressive stress,^{4,5} while material grown on SiC is typically under tension.^{5,6} We see in Fig. 1(a) that all spectra are dominated by FE_A and by D_0X , where the assignment of features was done in accordance with previous studies.^{3,7} It is clear in Fig. 1(a) that the energy of FE_A and, consequently, the energy of D_0X varies with each sample.

To interpret these data, we apply conventional elastic theory for the case of GaN films, after Edwards *et al.*⁶ Neglecting anisotropic relaxation, we can determine the relationship between the in-plane stress $\sigma_{xx} = \sigma_{yy} = \sigma_{11}$ and the in-plane ($\epsilon_{xx} = \epsilon_{yy} = \epsilon_{11} = \epsilon_{22}$) and out-of-plane ($\epsilon_{zz} = \epsilon_{33}$) strains from the known elastic constants of GaN.⁸ After Nye,⁹ we have $\{C\}^{-1} = \{S\}$ and $\epsilon_{ij} = S_{ijkl}\sigma_{kl}$. Assuming that $\sigma_{11} = \sigma_{22}$ and that all remaining $\sigma_{ij} = 0$ we find

$$\begin{aligned}\epsilon_{11} &= [C_{11} + C_{12} - 2(C_{13}^2/C_{33})]^{-1}\sigma_{11} \\ &= (4.18 \times 10^{-12} \text{ Pa}^{-1})\sigma_{11},\end{aligned}\quad (1a)$$

$$\epsilon_{33} = (-4.93 \times 10^{-12} \text{ Pa}^{-1})\sigma_{11}.\quad (1b)$$

The hydrostatic, and therefore the in-plane strain, can be obtained within an additive constant E_{A0} from the measured gap energy E_A and the deformation potential a according to

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FIG. 1. (a) PL spectra measured at temperature $T=2$ K for GaN layers grown by MOCVD on 6H-SiC substrates (solid lines). The layer thickness is indicated for each spectrum. The PL spectrum taken for an 80- μm -thick GaN layer grown by HVPE on sapphire substrate is shown by the dashed line. (b) The positions of the free A exciton (squares) and of the donor-bound exciton (circles) obtained from PL spectra are plotted vs the estimated in-plane stresses.

the empirical expression $E_A = E_{A0} + a\epsilon_H$, where $\epsilon_H = \Delta V/V = \epsilon_{11} + \epsilon_{22} + \epsilon_{33}$, $E_{A0} = 3.4764$ eV,¹⁰ and $a \approx -10$ eV. The data in Fig. 1(a) can then be expressed as shown in Fig. 1(b), where, in accordance with conventional wisdom, we see that the GaN layers grown on 6H-SiC are under tension with stress values varying from 1 to 3 kbar. The thick HVPE sample, as expected, is under in-plane compression with the FE_A energy at 3.4818 eV.

Results of time-resolved PL for GaN layers of different thickness are shown in Fig. 2. The PL decay curves were measured ($T=2$ K) at the peak position of FE_A and at the peak position of D_0X and are shown in Figs. 2(a) and 2(b), respectively. We see in Fig. 2(a) that the PL decays for FE_A all show similar behavior, with near exponential kinetics and recombination times about $\tau=40$ –50 ps under the lower excitation density of 100 mW/cm² [solid lines in Fig. 2(a)]. Under the higher excitation density of 2500 mW/cm² [dashed line in Fig. 2(a)] the recombination time for FE_A increases by 25%, which indicates a significant effect of non-radiative recombination channels. On the other hand, the recombination time for D_0X is practically independent of the excitation conditions. The difference between the values of the recombination time is less than 5% under high and low excitation density, respectively. The excitation power influences mainly the tail part of the PL decay curves, as shown in Fig. 2(b) by the solid and the dashed lines for the excita-

FIG. 2. (a) PL decay curves measured at 2 K for FE_A . The solid lines correspond to the data taken at the low excitation density of 100 mW/cm². The PL decay curve measured at the high excitation density of 2500 mW/cm² is shown by the dashed line. Open circles are the single-exponential fitting with PL decay time $\tau=40$ ps. (b) The PL decay curves measured at 2 K for D_0X at the excitation density of 2500 mW/cm² (solid lines). The PL decay curve taken at 100 mW/cm² is shown by the dashed line. Curves are shifted in vertical direction for clarity. The sample thickness is indicated for each plot.

tion density of 2500 and 100 mW/cm², respectively. The PL of D_0X demonstrates a typical near-exponential decay mechanism and we have found that the recombination times for D_0X have different values for different layers. The PL lifetime was evaluated for both FE_A and D_0X supposing a single-exponential decay $I(t) = I_0 e^{-t/\tau}$. An example of the fitting with $\tau=40$ ps is shown in Fig. 2(a) by open circles for the PL decay curve measured for the 1.9- μm -thick GaN layer. Taking into account the system resolution we estimate that the error of such extraction is less than 15%.

The PL lifetime τ includes both radiative lifetime τ_r and nonradiative lifetime τ_{nr} ($1/\tau = 1/\tau_r + 1/\tau_{nr}$). At low temperature nonradiative processes usually limit the recombination lifetime for free excitons. However, for donor-bound excitons we can estimate the radiative lifetime by extrapolation of τ to $T=0$ assuming that τ_r is temperature independent and that the nonradiative recombination rate is thermally activated according to an exponential law as described in Ref. 3. In Fig. 3(a) the temperature dependencies of the recombination lifetimes for D_0X and for FE_A are shown by circles and by open squares, respectively. One can conclude that the recombination lifetimes τ for the D_0X measured at 2 K correspond rather well to the radiative lifetimes τ_r .

In Fig. 3(b) the recombination lifetimes for FE_A (squares) and for D_0X (circles) measured for each GaN layer are plotted versus the photon energy of FE_A . The data are shown for the low temperature $T=2$ K. The upper axis is calibrated in terms of the in-plane stress σ_{xx} . We have observed an interesting fact; namely, that the PL decay times for D_0X increases with increasing FE_A (i.e., with decreasing

FIG. 3. (a) Recombination lifetimes are shown as a function of temperature for FE_A (squares) and for D_0X (circles). (b) The recombination lifetimes measured at $T = 2$ K for FE_A (squares) and for D_0X (circles) are plotted vs the low-temperature ($T = 2$ K) energies of FE_A . The upper axis corresponds to in-plane stress calculated for the GaN layers. The filled signs show the recombination lifetimes for FE_A and for D_0X in the HVPE grown GaN layer on sapphire substrate. The dashed lines are a guide for eye.

strain) for the layers under tension. For comparison we also plot (filled symbols) the recombination times of FE_A and of D_0X (from Ref. 3) for the HVPE grown GaN layer. From Fig. 3(b) it is clearly seen that D_0X recombination times vary rather significantly from ~ 60 ps in the most strained layer up to ~ 110 ps in the less strained layer. On the other hand we have not observed any difference for the recombination lifetime of FE_A in these samples.

We assume that D_0X has the same character in all measured structures since all of the samples were grown under similar conditions. Indeed, the material quality of the samples is comparable, as determined by complementary x-ray diffraction, scanning electron microscope, atomic force microscope, and PL measurements¹¹ and by the values of the recombination lifetime for FE_A . Thus it is reasonable to assume that the observed dependence of the recombination lifetime for D_0X on the position of FE_A is related to strain effects on the valence band states. Indeed, the radiative lifetime of D_0X is correlated with overlapping of the wave functions of the electron and hole.¹² Furthermore, we know that

the neutral bound exciton interaction involves an interaction between an outer hole with a two-electron state.¹³ This interaction could be directly related to the hole states involved (Γ_7 or Γ_9). Since the valence bands are rather close at the Γ point the hole wave function should have a mixed character. Thus, since we know that the band structure in GaN changes significantly with strain,^{6,14} it is plausible that we indirectly observe this change through the radiative lifetime for D_0X . With increasing tensional strain the energy splitting between the valence bands A and B decreases at our strain values.¹⁴ This means a reduction in the radiative lifetime due to an increased B character of the hole wave function, which in turn leads to a somewhat more extended mixed hole wave function, and an increased electron-hole overlap matrix element.¹² This explanation is consistent with our experimental data.

In conclusion, we have studied a series of strained wurtzite GaN epilayers of different thickness up to 4 μm . The structures were grown by MOCVD on 6H-SiC substrates with AlN buffer layers. From the energies of the free A exciton we have determined that the layers were under tension. The recombination lifetimes were measured for FE_A and for D_0X . We have found that the recombination lifetime for FE_A has the same value 40–50 ps in all the layers, whereas the recombination time for D_0X varies for different samples from 60 up to 110 ps. The recombination lifetimes for D_0X are dependent on the position of FE_A , i.e., the recombination lifetime increases with decreasing tensile strains in the layers.

- ¹ S. Nakamura, M. Senoh, N. Iwasa, and S. Nagahama, Jpn. J. Appl. Phys., Part 2 **34**, L797 (1995).
- ² S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto, and H. Kiyoku, Jpn. J. Appl. Phys., Part 2 **36**, L1059 (1997).
- ³ G. Pozina, J. P. Bergman, T. Paskova, and B. Monemar, Appl. Phys. Lett. **75**, 4124 (1999).
- ⁴ R. Dingle, D. D. Sell, S. E. Stokowski, and M. Ilegems, Phys. Rev. B **4**, 1211 (1971).
- ⁵ B. J. Skromme, H. Zhao, D. Waag, H. S. Kong, M. T. Leonard, G. E. Bulman, and R. J. Molnar, Appl. Phys. Lett. **71**, 829 (1997).
- ⁶ N. V. Edwards, S. D. Yoo, M. D. Bremser, T. W. Weeks, Jr., O. H. Nam, R. F. Davis, H. Liu, R. A. Stall, M. N. Horton, N. R. Perkins, T. F. Keuch, and D. E. Aspnes, Appl. Phys. Lett. **70**, 2001 (1997).
- ⁷ K. P. Korona, A. Wyszomolek, J. M. Baranowski, K. Pakula, J. P. Bergman, B. Monemar, I. Grzegory, and S. Porowski, Mater. Res. Soc. Symp. Proc. **482**, 501 (1998).
- ⁸ *Properties of Group III Nitrides*, edited by J. H. Edgar (IEEE, London, 1994).
- ⁹ J. F. Nye, *Physical Properties of Crystals* (Clarendon, Oxford, 1985).
- ¹⁰ K. Pakula, A. Wyszomolek, K. P. Korona, J. M. Baranowski, R. Stepniewski, I. Grzegory, M. Bockowski, J. Jun, S. Krukowski, M. Wroblewski, and S. Porowski, Solid State Commun. **97**, 919 (1996).
- ¹¹ N. V. Edwards, M. D. Bremser, R. F. Davis, A. D. Batchelor, S. D. Yoo, C. F. Karan, and D. E. Aspnes, Appl. Phys. Lett. **73**, 2808 (1998).
- ¹² G. D. Sanders and Y.-C. Chang, Phys. Rev. B **28**, 5887 (1983).
- ¹³ B. Monemar, U. Lindelfelt, and W. M. Chen, Physica B **146**, 256 (1987).
- ¹⁴ B. Gil, *Semiconductors and Semimetals*, edited by J. I. Pankove and T. D. Moustakas (Academic, San Diego, 1999), Vol. 57, p. 209.