Optical investigations of AlGaN on GaN epitaxial films

G. Steude[a)] and B. K. Meyer
I. Physikalisches Institut, Universität Giessen, D-35392 Giessen, Germany

A. Göldner and A. Hoffmann
Institut für Festkörperphysik der TU Berlin, Hardenbergstrasse 36, D-10623 Berlin, Germany

F. Bertram and J. Christen
*Abteilung Festkörperphysik, Otto-von-Guericke-Universität Magdeburg, PF 4120,
D-39016 Magdeburg, Germany*

H. Amano and I. Akasaki
*Department of Electrical and Electronic Engineering, Meijo University, 1-501 Shiogamaguchi,
Tempaku-ku, Nagoya 468, Japan*

We investigated coherently strained $Al_xGa_{1-x}N$/GaN heterostructures ($0 < x < 0.22$) grown by metalorganic vapor phase epitaxy on sapphire with photoluminescence (PL), reflexion and cathodoluminescence experiments. The energetic positions of the free A exciton as a function of the alloy compositions are deduced from temperature dependent PL and from reflexion measurements. We obtain a small bowing parameter and no evidence for a Stokes shift between absorption and emission. Compositional inhomogeneities are present, but the fluctuations are too small to be important for carrier localization. The broadening of the luminescence linewidth in the alloys can be described by statistical disorder of a random alloy. © *1999 American Institute of Physics.* [S0003-6951(99)03417-8]

Optoelectronic devices based on the group-III nitrides, AlN, GaN, and InN and their ternary alloys have a wide field of application because one can cover the visible to ultraviolet spectral range. In order to optimize the device performance the properties of the ternary alloys have to be understood and controlled. Since the lattice mismatch between AlN and GaN is 2.4% and for InN on GaN it is 11% strain effects (i.e., pseudomorphic versus strain relaxed growth) play an important role. They can lead to compositional fluctuations and eventually to phase separations. Quantum dot formation may result. Also the influence of piezoelectric field effects on the luminescent properties cannot be neglected.

We have recently reported on the excitonic luminescence of coherently strained AlGaN on GaN heterostructures and derived the excitonic band gap dependence on the Al molar fraction ($x < 0.22$) at room temperature. The deviation from a linear dependence was small and we obtained the nonlinear contribution (bowing parameter) to be 0.6 eV.[1] At low temperatures localized exciton emission dominates. The free A-exciton emission was only observable at elevated temperatures ($T > 100$ K) and was traced back to low temperatures by a fit to the temperature dependence of the band gap.[2] However, localization in random potentials caused by alloy disorder might influence the energetic position at low temperatures and conclusions on the presence or absence of a Stokes shift between absorption and emission cannot be derived from PL alone. We therefore extended these investigations towards reflexion, transmission, and absorption spectroscopy using calorimetric detection (CRS, CTS, CAS). Cathodoluminescence (CL) experiments were used to re-

solve eventual compositional inhomogeneities.

The films were grown by metalorganic vapor phase epitaxy (MOVPE) on sapphire (0001) substrates. In a first step a 2-μm-thick GaN film was grown on a 30-nm-low temperature deposited AlN buffer. On this GaN layer nominally undoped $Al_xGa_{1-x}N$ films with thicknesses between 320 and 750 nm were grown. The AlN molar fraction varied between $0 \leq x \leq 0.22$. More details especially about the determination of the composition can be found in Ref. 3. Photoluminescence was excited with the 248 nm line of an excimer laser. Details of the setup for calorimetric detection of reflexion, transmission, and absorption spectroscopy can be found in Ref. 4. 4 K cathodoluminescence measurements were performed in fully computerized scanning electron microscope. The spatial resolution is better then 50 nm. In the CL wavelength image (CLWI) mode the local emission wavelength is mapped at any point of a rectangular area which is scanned by the electron beam (for further details see Ref. 5).

In Fig. 1 the PL spectrum of an AlGaN epilayer with 22% Al content is shown starting from 4 up to 500 K. At temperatures around 100 K one notes the appearance of the free A-exciton emission which then maintains up to 500 K. In the range up to 22% Al-content, the dependence of band gap on temperature can be expressed by

$$E(T) = E(0) - \frac{BT^2}{(\Theta_D - T)}, \tag{1}$$

with one set of parameters $\beta = (4.7 \pm 0.2)*10^4$ eV/K and $\Theta_D = 960 \pm 40$ K. One clearly notes the lower peak positions at low temperatures where the emission of localized excitons takes over. The energetic difference is a measure of the localization energy which might originate from localiza-
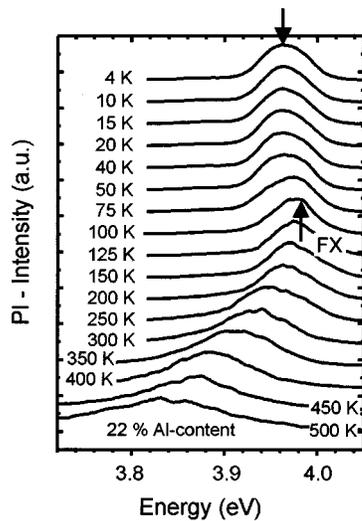
a)Electronic mail: guido.steude@expl.physik.uni-giessen.de

FIG. 1. Temperature dependence of the photoluminescence of an $Al_xGa_{1-x}N$ film with $x=0.22$. The arrow marks the transition from localized to free exciton emission.

FIG. 3. Cathodoluminescence wavelength imaging for an $Al_xGa_{1-x}N$ film with $x=0.22$ at $T=6$ K.

tion of the free exciton at neutral donors and/or from localization in random potential fluctuations caused by alloy disorder.[6]

In Fig. 2(a) we present CAS, CRS, and CTS spectra of a sample with 6% Al content. The measurements were performed at 47 mK. One can identify the signals from the A and B excitons of the underlying GaN at the band gap energy of around 3.5 eV. At higher energies the signal from the A exciton of the AlGaN film can be seen. In Fig. 2(b) we com-
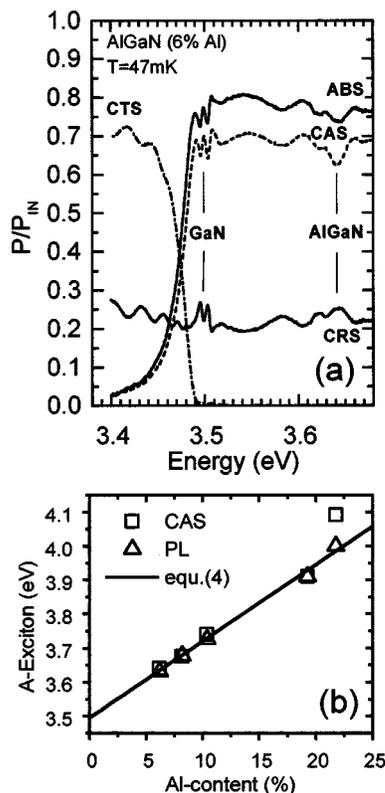

FIG. 2. (a) Calorimetric absorption, reflexion, and transmission measurements (CAS, CRS, CTS) on an $Al_xGa_{1-x}N$ film with $x=0.06$ at 47 mK. (b) The A-exciton line position as a function of Al contents [triangles: from photoluminescence; squares: from calorimetric measurement; drawn line: $E_g(x)$.
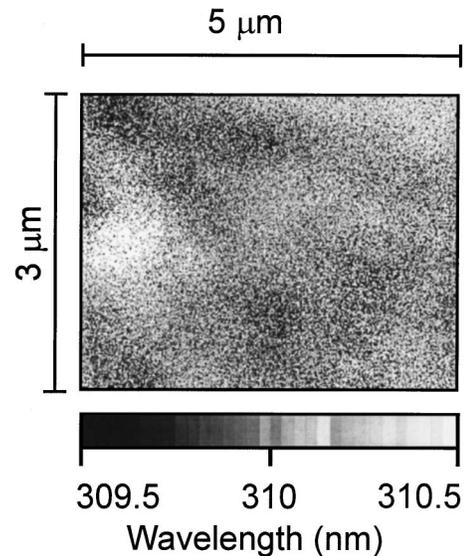
pare the line positions of the free A exciton from calorimetric measurements and PL by extrapolating to low temperatures using Eq. (1). One notes an almost perfect agreement. Small differences might be caused by compositional inhomogeneities which we tried to resolve by CL measurements. In Fig. 3 we present CLWI of the film with the highest Al content ($x=0.22$). On a scale of 3 times 5 μm^2 the spectral position of the luminescence is mapped. The position is visualized on a gray scale, darker areas mean emission at lower wavelength. There are certainly inhomogeneous regions on the scale of microns. One should, however, have in mind that the energetic positions differ only by some 10–15 meV whereas the total band gap shift for this composition is 0.5 eV. Translating to compositional fluctuations this is 2% of 22%.

Besides the energetic shift of the excitonic emission with increasing Al content the linewidth of the localized exciton luminescence increases from 14 meV for $x=0.06$ to 35 meV for $x=0.22$. This can be explained by alloy broadening. We compare the experimental values with a calculation based on a model introduced by Schubert *et al.*[7] The broadening is caused by a statistical occupation of the cation places Ga by Al and the alloy disorder is seen by the exciton. Therefore we need to consider the exciton volume and its Bohr radius. The exciton volume is given by

$$V_{\text{exc}} = \frac{4}{3}\pi\left(\frac{\epsilon_r}{m_r/m_0}a_B\right)^3, \qquad (2)$$

where ϵ is the dielectric constant in the alloy, m_r in units of m_0 is the exciton reduced mass ($1/m_e + 1/m_h$), and a_B the Bohr radius of the exciton. For ϵ we interpolated between GaN ($\epsilon=9.7$) and AlN ($\epsilon=6.3$). The same was done for the reduced mass and the Bohr radius. For the hole mass we used the theoretical value of $m_h=1.5$ without any variation whereas the electron effective mass was interpolated between $m_{e,\text{GaN}}=0.22m_0$ and $m_{e,\text{AlN}}=0.33m_0$ and neglected possible small anisotropies. This leads to a variation of the Bohr radius of the free exciton from 27 Å in GaN to 12 Å in AlN. The alloy broadening is given by
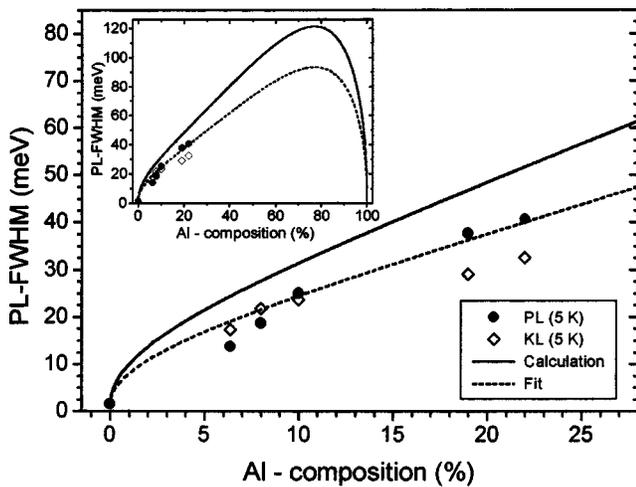
FIG. 4. The full width at half maximum of the localized exciton emission line in AlGaN. Full squares: PL data; open diamonds: KL data; drawn line: calculated using Eq. (3); dotted line: fit to the experimental data. Inset: expected behavior for the whole compositonal range.

$$\Delta E_{exc} = 2.36\sigma_E = 2.36\frac{dE_g}{dx}\left(\frac{x(1-x)}{KV_{exc}}\right)^{1/2}, \qquad (3)$$

dE_g/dx is the variation of the energy gap with composition, for which we used the analytical expression $E_g(x) = E_{g,GaN} + (c-b)x + bx^2$ with $c = E_{g,AlN} - E_{g,GaN}$ and $b = 0.6$ eV. For the band gaps we used 3.48 eV (GaN) and 6.2 eV (AlN). K is the density of cations in the crystal. The factor 2.36 accounts for Gaussian broadening.

In Fig. 4 we compare experiment and calculation. The maximum of broadening is reached for 80% Al content which is related to the considerable increase of the electron effective mass towards AlN and the decrease of the dielectric constant. Due to decreasing Bohr radius in AlGaN the excitons will see much more alloy disorder. Similar conclusions have been reached independently by Zubrilov *et al.*[8]

In CL measurements slightly different linewidths are observed due to the fact that the exciting spot size is smaller. In any case the experimental data are below the calculated curve. We, however, must have in mind that we are dealing in the experiments with localized excitons and not with free excitons for which the Bohr radius concept is valid. For neutral acceptor bound excitons which were treated in the framework of the pseudodonor model the influence of alloy broadening could be calculated. However, this model cannot be transferred to the neutral donor bound excitons or localized excitons, since it requires the knowledge of which particle of the exciton, electron, or hole is bound first.[9] Assuming exciton radii which are slightly larger, i.e., 32 Å for GaN and 15 Å for AlN one obtains a better fit to the experimental data, as shown by the dotted line in Fig. 4. Our data are in qualitative agreement with the results from Zubrilov *et al.*;[8] they are, however, not directly comparable because they analyzed 300 K data.

Our experimental results confirm that alloy broadening in this statistical model accounts for the linewidth and clustering is negligible at least for this composition range investigated. It is also in line with the wavelength imaging by CL presented in Fig. 3.

From x-ray data it was already concluded that AlGaN grew coherently on GaN resulting in a tensile stress in the AlGaN layers. It should, however, be less than 0.5% since strained and unstrained AlGaN layers have practically the same composition dependence of the band gap.[10] Our data support these conclusions. There is no evidence for a Stokes shift between absorption and emission and the bowing parameter is small. This is in contrast to strained InGaN on GaN heterostructures where a bowing parameter of 3.2 eV is found experimentally for $x < 0.2$ (Ref. 11) and the problems of compositional inhomogeneities and miscibility gaps are present.[12–14] In AlGaN for the alloy composition range $0 < x < 0.22$, which is also the technological relevant one for the realization of blue laser diodes, the films do much better.

In conclusion we reported on photoluminescence, calorimetric spectroscopy, and cathodoluminescence of $Al_xGa_{1-x}N$ on GaN layers for alloy compositions $0 < x < 0.22$. Small compositional inhomogeneities could be resolved, but will play a minor if not negligible role in carrier localization. The luminescence linewidth increases in the alloy as expected for a random alloy and we predict a maximum of 90 meV for the range between 70% and 80% Al. In contrast to InGaN/GaN pseudomorphic AlGaN/GaN single heterostructures with $x < 0.22$ show a small bowing parameter. There is an overall agreement in line positions of free exciton absorption and emission.

[1] G. Steude, D. M. Hofmann, B. K. Meyer, H. Amano, and I. Akasaki, Phys. Status Solidi B **205**, 7 (1998).

[2] G. Steude, D. M. Hofmann, B. K. Meyer, H. Amano, and I. Akasaki, Phys. Status Solidi A **165**, R3 (1998).

[3] T. Takeuchi, H. Takeuchi, S. Sota, H. Sakai, H. Amano, and I. Akasaki, Jpn. J. Appl. Phys., Part 2 **36**, L177 (1997).

[4] L. Podlowski, A. Hoffmann, and I. Broser, J. Cryst. Growth **117**, 698 (1992).

[5] J. Christen, M. Grundmann, and D. Bimberg, J. Vac. Sci. Technol. B **9**, 2358 (1991).

[6] B. Monemar, Phys. Rev. B **10**, 676 (1974).

[7] E. F. Schubert, E. O. Göbel, Y. Horikoshi, K. Ploog, and H. J. Queisser, Phys. Rev. B **30**, 813 (1984).

[8] A. S. Zubrilov, D. V. Tsvetkov, V. I. Nikolaev, and I. P. Nikitina, Semiconductors **30**, 1069 (1996).

[9] K. Oettinger, D. M. Hofmann, A. L. Efros, B. K. Meyer, M. Salk, and K. W. Benz, J. Appl. Phys. **71**, 4523 (1992).

[10] D. K. Wickenden, C. B. Bargeron, W. A. Byrden, J. Miragliova, and T. J. Kistenmacher, Appl. Phys. Lett. **65**, 2024 (1994).

[11] M. D. McCluskey, C. G. Van de Walle, C. P. Master, L. T. Romero, and N. M. Johnson, Appl. Phys. Lett. **72**, 2725 (1998).

[12] I.-H. Ho and G. B. Stringfellow, Appl. Phys. Lett. **69**, 2701 (1996).

[13] N. A. El-Masry, E. L. Piner, S. X. Liu, and S. M. Bedair, Appl. Phys. Lett. **72**, 40 (1998).

[14] D. Behr, J. Wagner, A. Ramakrishnan, H. Obloh, and K.-H. Bachem, Appl. Phys. Lett. **73**, 241 (1998).