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Quantized states in $Ga_{1-x}In_xN/GaN$ heterostructures and the model of polarized homogeneous quantum wells

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Centers of spontaneous and stimulated light emission in $Ga_{1-x}In_xN/GaN$ active layers as analyzed in luminescence and photoreflection spectroscopy are modeled under the assumption of polarized laterally homogenous quantum wells. In perturbation to the band structure of wurtzite GaN including experimental polarization fields and band-gap bowing the spectrum of interband transitions is calculated for $0<x<0.2$. We predict the first transition between quantized electron and hole states to lie close to a maximum in photoreflection and close to the energy of stimulated emission. The level of the main luminescence under low excitation cannot be described in this single-particle picture. These results allow a quantitative treatment of that level, e.g. in models of lower dimensionality.

Performance of group-III nitride light emitters is poised to take the next big leap as soon as the electronic band structure in quantum wells will be determined and respective interband transitions are identified.[1,2] A lingering puzzle is the very nature of the light-emitting centers in the active layer of $Ga_{1-x}In_xN/GaN$ quantum wells. In various studies of optical spectroscopy, evidence was found for a continuum of states or levels with varying energy.[3–7] This has led to models of transient photocarrier localization into potential minima of reduced dimensionality. It, therefore, was proposed that zero-dimensional centers were formed within the two-dimensional quantum wells by means of large potential fluctuation[3–7] as the result of strong alloy fluctuation[8] and a tendency towards phase separation.[9–11] Such effects are well understood in other In-containing alloys and also for $Ga_{1-x}In_xN$ alloys they are known to occur under certain growth or annealing conditions especially at high temperatures.[9]

Alternative models, however, have been developed[12–14] that deny the necessity of such quantum dots to describe the observations in high-quality $Ga_{1-x}In_xN/GaN$ material optimized for laser diode performance with emission wavelengths below 450 nm. In this study we investigate in how far results of photoluminescence (PL) and photoreflection (PR) spectroscopy in $Ga_{1-x}In_xN/GaN$ quantum wells[15] can be described within the model of polarized laterally homogenous quasi-two-dimensional quantum wells. These results shall also provide an important developmental step towards accurate models of zero-dimensional quantum dots.

Devices of high performance make use of the uniaxial wurtzite form of group-III nitrides, which due to the lack of inversion symmetry along the unique c axis and partly ionic bonding conditions exhibits strong electric polarization properties.[16] In typical epitaxial growth, i.e., Ga face, this axis coincides in direction and polarity with the growth direction z. At heterointerfaces the discontinuity of the polarization induces huge fixed polarization charges that range from 2.6×10^{13} cm^{-2} in experiment[14] to 8.6×10^{13} cm^{-2} in theory[16] when extrapolating to InN on GaN. Polarization is both a function of the constituent alloy and its state of strain. We base our model on the directly determined electric-field values in the quantum well[17] and the alloy band-gap energy as derived from thin-film material.[18]

Sets of pseudomorphic $Ga_{1-x}In_xN/GaN$ multiple quantum wells (QW's) with variable InN fraction x have been studied in PL and PR spectroscopy as reported elsewhere.[15,19] A 325 nm laser was used for either photoexcitation at a power density of 1–100 W/cm^2 or photomodulation ($\approx$0.1 W/cm^2). Pulsed high excitation density $\leqslant 5$ mJ/cm^2 was achieved at 337 nm. Nominally undoped layers have been grown by metal organic vapor phase epitaxy and consist of $L_w=30$ Å $Ga_{1-x}In_xN$ wells embedded in 60 Å GaN barriers atop a 2 μm GaN epilayer on sapphire using low-temperature deposited buffer layers of AlN.[15,20] Films have been optimized for homogeneity in terms of specular reflectance, x-ray diffraction, and luminescence peak energy. The possible advantages of material with lateral inhomogeneities have been discussed in the literature.[3,5] For the sake of a simplified spectroscopic analysis, however, we limit this study to material with high lateral homogeneity.[1] All experimental and calculated data refer to room-temperature values.

PL and PR of three samples with identified composition in the relevant composition range $x=0.12$, 0.15, and 0.18 are presented in Fig. 1.[19] The spectra of stimulated emission under pulsed UV excitation are included.[21] As reported luminescence closely corresponds to the lowest maximum in the PR spectrum.[15] This supports the theory that in this homogenous material luminescence originates in discrete levels that also form critical points in the joint density of states (DOS) as detected by the absorption-type PR. A number of interband transitions can be labeled at PR extrema as indicated by ticks below the spectra. Narrow oscillations in N_0 mark the GaN barrier band-gap energy. The oscillations with extrema

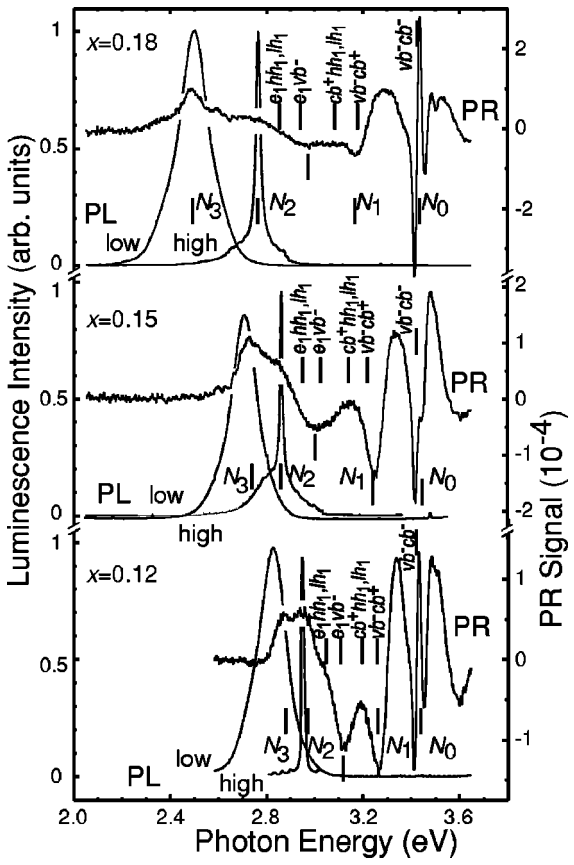

FIG. 1. Photoreflection and photoluminescence (label *low*) of $Ga_{1-x}In_xN/GaN$ active layers in comparison with model results for homogeneous polarized QW's. There are no adjustable parameters. Considered transitions (upper ticks) are in good agreement with experimental peak positions (lower ticks) except the lowest one in N_3. A PR maximum in N_2 closely marks the first electron (e) to first-hole (hh, lh) transitions in the polarized well. Also at this energy stimulated emission occurs under high excitation density (label *high*). The causal connection for this is not obvious at present. A PR minimum appears near the low-lying bound-to-free transition e_1vb^-. The electric field is derived from Franz-Keldysh oscillations with extrema above N_1. Its dipole across the well defines transition cb^+vb^- in N_1. N_0 is the barrier band gap.

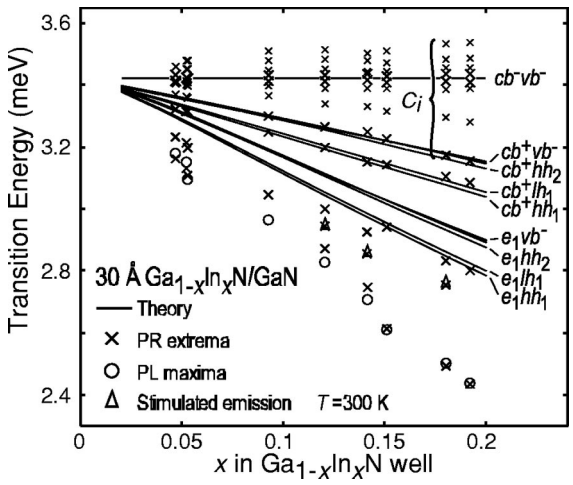

FIG. 2. Collected peak positions of photoreflection and photoluminescence in 11 $Ga_{1-x}In_xN/GaN$ quantum-well samples with variable composition from Ref. 15 together with theory results. The well composition has been determined through an x-ray analysis for three samples. Values for the remaining samples have been inferred from scaling of the polarization dipole. Despite the limitations of the model we find good agreement for the higher and excited states when experimental band-gap bowing and polarization dipole are considered and lateral homogeneity is assumed.

in C_i above N_1 as labeled in Ref. 15 and Fig. 2 have been identified as Franz-Keldysh oscillations in the presence of the polarization field across the well[17] and allow for an accurate determination of the field strength: $F=0.55$ MV/cm ($x=0.12$), 0.60 MV/cm (0.15), and 0.82 MV/cm (0.18), respectively. The composition has been derived in a dynamical x-ray rocking analysis using high-order satellite diffraction maxima.[20] These value pairs serve as input parameters in the band structure model described below.

The field increases linearly with the InN fraction as a result of the piezoelectric properties of the strained system. The splitting of N_0 and N_1 reflects the asymmetric barrier heights of the polarized QW or the multi-interface band offset across the well and scales with the field according to $\Delta E=FeL_w$ (electron charge e).[17] Field or splitting, therefore, serve as a good scale for further samples with unknown composition. Figure 2 recollects the results of a total of 11 samples with variable composition versus the so determined field strength rescaled to x along the field of the samples in Fig. 1. The marked levels N_2 and N_3 appear to replicate the polarization controlled splitting of N_0 and N_1 into a Starklike ladder.[15]

The electronic band structure in wurtzite group-III nitrides has been derived in theory by full potential linearized muffin-tin orbitals[22] and first-principles calculations in the literature.[2,23] Binary bulk components GaN and AlN have so been described to great detail while the problem of an inaccurate band gap energy has hampered progress for InN. Relative band offsets have been studied in experiment[24] and in theory.[25,26] The subaspect of valence subbands in QW's in absence of any polarization has been considered in Ref. 23 while models for quantized valence and conduction-band states[13,27,28] in the presence of electric fields are limited to the lowest interband transitions.

The dispersion of band-edge states in $Ga_{1-x}In_xN$ as a function of composition and biaxial strain has not been established. We therefore base our model primarily on parameters of GaN and use linear interpolations to values of InN where available as described in the following: We use GaN values for the theoretical effective mass parameters for the electron (e), heavy-hole (hh), light-hole (lh), and crystal-field split-off hole (ch).[22] We include the strong asymmetry of mass values along and perpendicular to the z axis as provided in that data. Linear interpolations of GaN and InN values are used for the lattice constants in strain-free alloys[18] for the ratio of the elastic constants[29] and the theoretical deformation potentials[26] of the valence and conduction bands. The relative InN/GaN band offset is taken from theory.[26] Values are summarized in Table I. The DOS band-gap energy[18] and the strength of the piezoelectric field are taken from experiment. This is in contrast to some models in the literature where the field strength was a variable.[13,27,28]

TABLE I. Values of model parameters as cited in the text.

Effective mass	m^*/m_0	$k\|z$	$k\perp z$
	e	0.23	0.23
	hh	2.00	0.34
	lh	1.19	0.35
	ch	0.17	1.27
		GaN	InN
Absolute volume	$\partial E/\partial \ln \Omega$		
deformation	d	−4.2 eV	−3.0 eV
potential	a_v	2.0 eV	1.7 eV
	a_g	−8.0 eV	−5.0 eV
Ratio of elastic constants	$2C_{13}/C_{33}$	0.5 10	0.821

Schrödinger and Poisson equations were solved self-consistently for electron states and hole states. Electron-electron as well as electron-hole many-particle interactions are not considered. Fixed polarization charges were assumed at the respective interfaces to the well. Barriers are assumed to be field-free. Figure 3 shows the band structure diagram for $x=0.12$. Combining the results of quantization energies E_{ei}, E_{hhi}, E_{lhi}, and E_{chi} we obtain sets of theoretical interband transition energies as indicated by ticks in Fig. 1 (above spectra). For an enhanced clarity of the result we limit ourselves to transitions $\Delta i=0$, where i is the ordinal number of the hole or electron envelope subband wave functions. We also account for transitions into the continuum of valence band vb and conduction-band cb. Due to the strong asymmetry in polarized QW's we distinguish the edges of those bands in positive (vb^+, cb^+) and in negative z direction (vb^-, cb^-). Transition energies in dependence of x are given by solid lines in Fig. 2.

Within the scope of the present single-particle model PL maxima at low excitation density appear below the expected level of the fundamental interband transition $e1hh1$ of the quantum well between the first quantized electron state e_1 and the first quantized heavy-hole state $hh1$. The latter, however, is marked near a further distinct PR maximum in N_2. This energy also closely coincides with the energetic level of the stimulated emission in all three cases of $x=0.12$, 0.15, and 0.18. Considering possible effects of spectral shifts under high photoexcitation density near the threshold to stimulated emission, the present coincidence cannot be taken as a positive identification of the level of stimulated emission. Within the wide spectral range covered here $e1hh1$, however, is the best approximation. At higher energies a strong minimum in PR in a falls close to the level e_1vb^+ expected for the lowest bound-to-free transition of the first electron level to the valence band-edge or weakly bound higher order hole states.

It is due to the large polarization dipole that these levels appear at such low energy. The splitting of heavy and light hole states cannot be observed in our experimental data. To test the reliability of the calculation we varied the input parameters. The experimental strain dependence of the band-gaps[30] can be reproduced by a scaling of the deformation potentials by a factor of 0.7. This will lower the predicted $e1hh1$ level by some 40 meV. However, for the sake of consistency we refrain from such minor corrections in this general picture. The edge for transitions between resonant states of conduction-band cb^+ and valence band vb^- by default coincides with N_1. Extrema C_i are part of the Franz-Keldysh oscillations. The agreement of PL and PR maxima in N_3 reveals a discrete level in the joint density of states below $e1hh1$ that is not described within the single-particle picture for any reasonable set of parameters. The splitting of N_2 and N_3 parallels that of N_0 and N_1 giving rise to the assumption of higher order interactions[15] in the presence of the polarization charges. Models proposing inclusions of regions of high In content cannot be supported in our homogeneous materials. The present result reveals that in contrast to N_2 the discrete level in N_3 deserves further special attention. A competition between both recombination processes could be a key to explain the high threshold densities for stimulated emission $I_{th}=0.072$ mJ/cm^2 ($x=0.12$), 0.47 mJ/cm^2 ($x=0.15$), and 4.7 mJ/cm^2 ($x=0.18$).[21]

Our model finds that the DOS as expressed in optical absorption as low as 3.850 eV (435 nm) can be described by polarized homogenous two-dimensional quantum wells when InN fractions up to $x=0.18$ are considered. Within this framework stimulated emission energies as low as 2.761 eV (449 nm) lie close to the predicted levels of the fundamental $e1hh1$ interband transition in the presence of large piezoelectric polarization. We find distinct and well-defined inter-

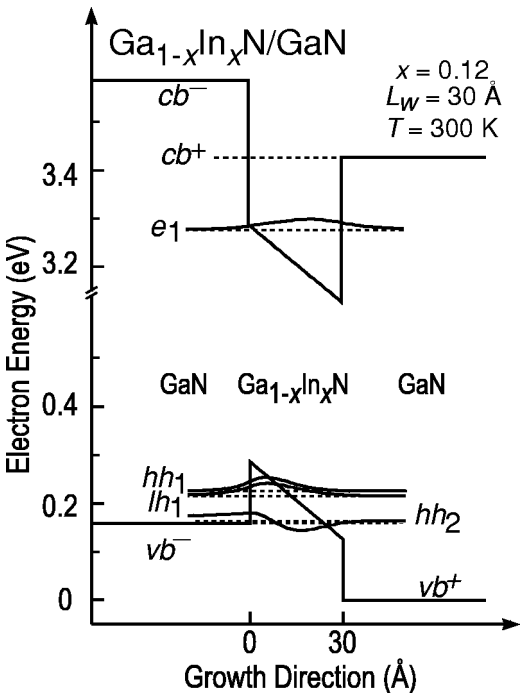

FIG. 3. Calculated level scheme of quantized states in a homogenous polarized 30 Å $Ga_{0.88}In_{0.12}N$/GaN quantum well of wurtzite in the presence of a piezoelectric field of 0.55 MV/cm with low index levels of electron (e), heavy-hole (hh), and light-hole (lh). Crystal-field split-off hole (ch) states are found to be in resonance with the barrier valence band. The wave functions are superimposed. The polarization dipole across the well offsets the continuum band edges. In this case an emission energy as low as 3.050 eV (407 nm) must be expected from a transition between first quantized electron and heavy-hole states $e1hh1$.

band transition energies in theory that correspond in energy to characteristic absorption edges and luminescence bands except for the lowest one. We so assign the luminescence in the limit of high excitation density and stimulated emission to the transition between first quantized electron states and first quantized heavy- and light-hole states. Luminescence in the limit of low excitation density in turn is found to originate within a center of discrete energy in the joint DOS that is not described within this model. Given the vast number of unsolved questions and apparent inconsistencies encountered in the study of GaInN/GaN quantum wells in the literature, the present results provide a clear guideline for the level assignment and a point of reference for the treatment of the luminescence at low excitation density. Therefore a model of laterally homogenous, two-dimensional polarized quantum wells based on established experimental and theoretical material parameter can well describe both emission and absorption data except its lowest level in material optimized for homogeneity.

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[1] I. Akasaki and H. Amano, Jpn. J. Appl. Phys., Part 1 **36**, 5393 (1997).

[2] For a review see M. Suzuki and T. Uenoyama, in *Properties, Synthesis, Characterization, and Applications of Gallium Nitride and Related Compounds*, edited by J. Edgar, T. S. Strite, I. Akasaki, H. Amano, and C. Wetzel (INSPEC/IEE, London, 1999), p. 155.

[3] S. Chichibu, M. Arita, H. Nakanishi, J. Nishio, L. Nishio, Y. Kokuban, and K. Itaya, J. Appl. Phys. **83**, 2860 (1998).

[4] S. Chichibu, T. Azuhata, T. Sota, and S. Nakamura, Appl. Phys. Lett. **70**, 2822 (1997).

[5] Y. Narukawa, Y. Kawakami, M. Funato, S. Fujita, S. Fujita, and S. Nakamura, Appl. Phys. Lett. **70**, 981 (1997).

[6] Y. Narukawa, Y. Kawakami, S. Fujita, S. Fujita, and S. Nakamura, Phys. Rev. B **55**, R1938 (1997).

[7] Y. Narukawa, Y. Kawakami, S. Fujita, and S. Nakamura, Phys. Rev. B **59**, 10 283 (1999).

[8] C. Kisielowski, Z. Liliental-Weber, S. Nakamura, Jpn. J. Appl. Phys., Part 1 **36**, 6932 (1997).

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

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

[11] R. Singh, D. Doppalapudi, T. D. Moustakas, and L. T. Romano, Appl. Phys. Lett. **70**, 1089 (1997).

[12] T. Takeuchi, S. Sota, M. Katsuragawa, M. Komori, H. Takeuchi, H. Amano, and I. Akasaki, Jpn. J. Appl. Phys., Part 2 **36**, L382 (1997).

[13] T. Takeuchi, C. Wetzel, S. Yamaguchi, H. Sakai, H. Amano, I. Akasaki, Y. Kaneko, S. Nakagawa, Y. Yamaoka, and N. Yamada, Appl. Phys. Lett. **73**, 1691 (1998).

[14] C. Wetzel, T. Takeuchi, H. Amano, and I. Akasaki, J. Appl. Phys. **85**, 3786 (1999).

[15] C. Wetzel, T. Takeuchi, H. Amano, and I. Akasaki, Jpn. J. Appl. Phys., Part 2 **38**, L163 (1999).

[16] F. Bernardini, V. Fiorentini, and D. Vanderbilt, Phys. Rev. B **56**, R10 024 (1997).

[17] C. Wetzel, T. Takeuchi, H. Amano, and I. Akasaki, Phys. Rev. B **61**, 2159 (2000).

[18] C. Wetzel, T. Takeuchi, S. Yamaguchi, H. Katoh, H. Amano, and I. Akasaki, Appl. Phys. Lett. **73**, 1994 (1998).

[19] C. Wetzel, T. Detchprohm, T. Takeuchi, H. Amano, and I. Akasaki, J. Electron. Mater. **29**, 252 (2000).

[20] H. Sakai, T. Takeuchi, H. Amano, and I. Akasaki, Rev. Laser Eng. **25**, 510 (1997).

[21] H. Sakai, T. Takeuchi, S. Sota, M. Katsuragawa, M. Komori, H. Amano, and I. Akasaki, J. Cryst. Growth **189**, 831 (1998).

[22] Kwiseon Kim, W. R. L. Lambrecht, B. Segall, and M. Van Schilfgaarde, Phys. Rev. B **56**, 7363 (1997).

[23] M. Suzuki, T. Uenoyama, and A. Yanase, Phys. Rev. B **52**, 8132 (1995).

[24] C. Manz, M. Kunzer, H. Obloh, A. Ramakrishnan, and U. Kaufmann, Appl. Phys. Lett. **74**, 3993 (1999).

[25] Su-Huai Wei and A. Zunger, Appl. Phys. Lett. **69**, 2719 (1996).

[26] C. G. van de Walle and J. Neugebauer, Appl. Phys. Lett. **70**, 2577 (1997).

[27] H. Kollmer, Jin Seo Im, S. Heppel, J. Off, F. Scholz, and A. Hangleiter, Appl. Phys. Lett. **74**, 82 (1999).

[28] H. S. Kim, J. Y. Lin, H. X. Jiang, W. W. Chow, A. Botchkarev, and H. Morkoc, Appl. Phys. Lett. **73**, 3426 (1998).

[29] A. F. Wright, J. Appl. Phys. **82**, 2833 (1997).

[30] A. Shikanai, T. Azuhata, T. Sota, S. Chichibu, A. Kuramata, K. Horino, and S. Nakamura, J. Appl. Phys. **81**, 417 (1997).