PIEZOELECTRIC LEVEL SPLITTING IN

GaInN/GaN QUANTUM WELLS

C. Wetzel, T. Takeuchi, H. Amano, and I. Akasaki

High Tech Research Center and Department of Electrical and Electronic Engineering,
Meijo University, 1-501 Shiogamaguchi, Tempaku-ku, Nagoya 468-8502, Japan

Cite this article as: MRS Internet J. Nitride Semicond. Res. 4S1, G3.66(1999)

ABSTRACT

Identification of the electronic band structure in AlInGaN heterostructures is the key issue in high performance light emitter and switching devices. In device-typical GaInN/GaN multiple quantum well samples in a large set of variable composition a clear correspondence of transitions in photo- and electroreflection, as well as photoluminescence is found. The effective band offset across the GaN/GaInN/GaN piezoelectric heterointerface is identified and electric fields from 0.23 - 0.90 MV/cm are directly derived. In the bias voltage dependence a level splitting within the well is observed accompanied by the quantum confined Stark effect. We furthermore find direct correspondence of luminescence bands with reflectance features. This indicates the dominating role of piezoelectric fields in the bandstructure of such typical strained layers.

INTRODUCTION

Heterostructures of GaInAlN alloys cover a wide range of electronic band gap energies and in combination with their physical stability provide an ideal wide bandgap system that in contrast to the family of SiC allows for advanced bandgap engineering over a wide energy range. Along with this advantage comes the challenge of a large lattice mismatch between the binary constituents and large biaxial stress in heteroepitaxy is the immediate consequence. Yet, owing to a great mechanical stability, mismatch of up to 2 or 3 % is readily supported in GaInN films of 40 nm thickness [1,2]. As we have shown in x-ray k -space mapping of both lattice constants a , within the growth plane, and c , along the growth direction, pseudomorphic growth can be achieved in $\text{Al}_y\text{Ga}_{1-y}\text{N}$ for $y < 0.25$ (thickness 500 nm) and $\text{Ga}_{1-x}\text{In}_x\text{N}$ $x < 0.2$ (thickness 40 nm) [1].

Biaxial strain in wurtzite with partly ionic bonding directly lead to large piezoelectric effects. This is evidenced directly by strong Franz-Keldysh oscillations (FKOs) in strained GaInN films [3,4,5] and by a quantum confined Stark effect in the luminescence shift of GaInN/GaN quantum wells [6]. Similar results have been observed in AlGaIn/GaN quantum wells [7]. While early piezoresistive measurements indicate very large piezoelectric coefficients [8] summarized in the quasi-cubic coefficient $e_{14} = 0.56 \text{ C/m}^2$ and even higher values are predicted in first principles calculations $e_{14} = 0.79 \text{ C/m}^2$ [9] we derive more modest values of $e_{14} = 0.1 \text{ C/m}^2$ from the interpretation of FKOs [5]. These smaller values are also in line with a trend of other compounds versus their ionicity [10]. The immediate question is the role these effects play in the unexpected properties of GaInN/GaN heterostructures and devices. To this end we here perform a photoreflection (PR), electroreflection (ER) and photoluminescence (PL) analysis of a series of device-typical $\text{Ga}_{1-x}\text{In}_x\text{N/GaN}$ multiple quantum well structures.

EXPERIMENTAL

Pseudomorphic $\text{Ga}_{1-x}\text{In}_x\text{N}/\text{GaN}$ heterostructures were grown along the c -axis by metal organic vapor phase epitaxy (MOVPE) on sapphire using low temperature deposited AlN buffer layers [6]. Samples consist of 5 sequences of nominally undoped $L_z=3$ nm $\text{Ga}_{1-x}\text{In}_x\text{N}$ wells embedded in 6 nm GaN barriers. The maximum composition is estimated to be $x = 0.2$. At this barrier width coupling of states between the wells is strongly suppressed. The set is grown either directly on 2 μm GaN or embedded in a GaN pn -junction with the p -side and a transparent contact on top. For reflection measurements we used a Xe white light source and a 325 nm 40mW HeCd laser for modulation (PR). The same laser was used for PL. In ER a sinusoidal voltage of 0.2 V_{pp} at 2 kHz and a variable offset was applied to modulate reflection in the pn -diode sample. All experiments were performed at room temperature.

PHOTOREFLECTION AND LUMINESCENCE IN GaInN/GaN MQW

PL and PR on nine samples with different well composition are presented in Fig. 1 in the

Figure 1 Photoreflection and photoluminescence of strained 3 nm GaInN/6nm GaN MQWs for 9 different compositions. Associated features are connected by dashed lines and grouped in features $C_0 \dots C_4$ and $N_0 \dots N_3$. In all samples a PR contribution appears close to the PL maximum. Interpreted electric field values are indicated on the right.

sequence of the PL peak energy. A series of narrow oscillations arbitrarily labeled $C_0 \dots C_4$ appears in the range of 3.2 – 3.7 eV range. Even sharper modulation appears near 3.42 eV (for the present purpose labeled N_0). A series of weaker but broad PR contributions $N_1 - N_3$ appears at lower energy the lowest of which has its maximum very close to the PL peak energy of the respective sample. This finding is in contrast to results by Chichibu *et al.* [11] where PR signal can be identified only at higher energies. Those levels would possibly correspond to levels N_1 or N_2 in our samples. A different signal amplitude may have contributed in this discrepancy. From the clear signature of N_3 , both in PL and PR, we propose that this PL originates in a well defined electronic level rather than a logarithmic edge of a randomly distributed property such as proposed in earlier work.

Figure 2 Interpretation of PR extremas C_i close to the GaN barrier bandgap. A good linear approximation indicates the nature of Franz-Keldysh oscillations and electric fields values are derived.

termination and layers of native oxide in general could affect the assignment of reflection data to the properties of the volume material. For this purpose we have studied solvent cleaned surfaces of GaN layers in angular resolved photoelectron spectroscopy [12]. Even without any thermal treatment we found that films are merely covered by one or two monolayers of oxygen only. Furthermore a perfectly hexagonal crystal structure of GaN is found up to the top-most atomic layers. This indicates, that reflectivity properties should not be affected by such layers in GaN. FKOs appear in reflectivity in the vicinity of an interband transition between states of carriers that are free to move along an electric field, e.g., near a three dimensional critical point in the joint DOS with fields applied along the normal of the layers. This is typically the case in bulk material or in low dimensional structures at energies above the quantum well. In the approximation proposed by Aspnes [13] the separation of oscillation extrema in $E_i = E(C_i)$ corresponds to the electro-optical energy $\hbar\Theta$ and to the electric field. Fig. 2 plots $4/(3\pi) (E_i - E_0)^{3/2}$ versus the extremum index i . Within each set points can be well approximated by straight lines. Note that according to the approximation scheme C_0 should be the origin of the linear interpolation. In this experiment the value of C_0 , however is not better known than any other point in the linear approximation and C_0 can not act as the origin of the interpolation. The slope of the interpolation corresponds to $(\hbar\Theta)^{3/2}$ and to the electric field $F = (\hbar\Theta)^{3/2} (2\mu)^{1/2} / (e\hbar)$. Herein $\mu = 0.2 m_0$ is the joint effective DOS mass assumed to be constant at the GaN value. The derived field values are indicated as labels in Fig. 1. Fields span a large range from $F = 0.23$ to 0.90 MV/cm and should directly reflect the piezoelectric field within the quantum wells. According to the interpretation of FKOs the three dimensional critical point would be associated closely to C_0 somewhere between the minimum and the maximum below in N_1 . This level $E_{3d} = (E(C_0) + E(N_1))/2$ has an apparent binding energy $E_{loc} = E(N_0) - E_{3d}$ with respect to the

The sharp oscillation in N_0 is attributed to excitons in the GaN barriers or the GaN epilayer underneath the MQW. The splitting in the order of 30 meV into the different excitons is below the current interest of our interpretation. Oscillations in the vicinity of N_0 , namely $C_0 \dots C_4$ strongly resemble FKOs above a critical point in the joint density of states (DOS) in the presence of a large electric field F . One minimum is close to N_0 and a distortion of both signals must be expected within some range around N_0 . The coexistence of excitonic features of GaN in N_0 and such FKOs indicate that the electric field is limited to the range of the GaInN quantum wells.

In other systems it has been demonstrated that the interpretation of PR data may involve a large number of parameters to accurately describe the observations. Especially surface

excitonic bandgap in the GaN barrier N_0 . This value also increases with x and is plotted in Fig. 3 versus the derived electric field values. We indeed observe a clear linear correlation and an inverse slope parameter of $E_{loc}/F \approx \Delta E_{loc}/\Delta F = 3.1 \times 10^{-9}$ eV m/V which defines an effective dipole. The value very closely matches the dipole of an elementary charge e in the piezoelectric field F across the well with $L_z = 3$ nm. We consequently propose that E_{loc} corresponds to the effective band offset across the heterointerface of each quantum well GaN/GaInN/GaN. This direct correspondence can be used to accurately determine either electric fields, well width or strain [14]. At lower energy the PR signal reveals two signatures labeled N_2 and N_3 that for increasing x split into two clearly separated levels. PL is found to follow the lower one in energy N_3 . At present parameters of the quantum well system are not sufficiently established as to make sufficient accurate predictions on the levels of the individual quantized states.

ELECTROREFLECTION IN A MQW *pn*-JUNCTION

In order to reveal more details on this splitting we performed electroreflectance spectroscopy of a MQW structure embedded in an *pn*-junction. Fig. 4. presents the results obtained under variable DC bias voltages. Due to the field induced by the *pn*-junction, the condition of a +2.5 V bias roughly corresponds to the case of the MQW wells studied above. Again several transitions are identified that lie close to levels previously labeled N_0 , N_1 and N_2 . Upon driving the *pn*-junction into the blocking regime and increasing the reverse bias level N_0 shifts to lower energy while levels N_2 and N_3 appear to merge.

The shift of N_0 can be interpreted as the electric field induced effective bandgap shrinkage caused by the Franz-Keldysh effect. Assignment of the origin of the observed signal from within the structure is not very clear. Besides the layers of the barriers also the adjacent doped contact

Figure 3 Correlation of derived electric field and apparent localization energy or effective band offset across the GaN/GaInN/GaN heterointerface.

regions may contribute in this signal. Due to high impurity concentrations doped layers, however, are less likely to produce a clear feature at the band edge. Assuming an origin right within the barriers of the MQW structure an effective field of 0.43 MV/cm can be estimated for the highest reverse voltages. Levels N_2 and N_3 must be associated with the quantized states within the QW. The merging of those levels clearly shows to be controlled by the applied electric field. Takeuchi *et al.* [6] have demonstrated in a similar structure that the PL peak energy also shows a strong dependence on the bias voltage. In that work a successive blue shift was observed for the PL under increasing reverse voltage and attributed to the quantum confined Stark effect (QCSE). Assuming a simple Stark splitting of levels N_2 and N_3 a field of 0.42 MV/cm corresponds to +2V bias in very good agreement with the shift of N_0 . Comparing with the PL results in Fig. 1 this level should be associated with N_3 and the effective splitting with respect to N_2 could be

Figure 4 Electoreflection in MQW pn-diode under variable (reverse) bias. Extrema closely corresponding to levels N_0 , N_2 , and N_3 in PR are identified. N_0 shifts in the increasing electric field while N_2 and N_3 merge indicating their field controlled splitting and a finite piezoelectric field for open terminal conditions.

This result also suggests that splitting of N_2 and N_3 in Fig. 1 without applied bias voltages is also controlled by the piezoelectric field. In Fig. 1, where spectra are plotted in the sequence of PL energy or attributed x , all levels N_0 , N_1 , N_2 and N_3 appear to originate in one point. In the ER experiment, however, levels clearly approach different points. This is well understood, when considering, that in the ER experiment, only the electric field is varied, while in the PR series, the entire sample structure is changed inducing the combined effects of well depth, quantization energies, and piezoelectric fields associated with the variable strain. As shown in the interpretation of the oscillations C_i , splitting of N_0 and N_1 is controlled by the electric field. In the result of the ER level splitting of N_2 and N_3 are also controlled by the electric field [15]. This strongly suggests, that the electric field plays an important role in the entire sequence of levels N_0 , N_1 , N_2 , and N_3 as seen in the PR. Work on the details of the full interpretation are currently underway.

SUMMARY

A detailed analysis of the electronic bandstructure in GaInN/GaN multiple quantum wells was performed by photoreflection and electoreflection spectroscopy. Franz-Keldysh-like oscillations are observed near the GaN band edge corresponding to large electric fields of 0.23 -- 0.90 MV/cm. The field increases with decreasing PL energy in correlation with the InN-fraction in the wells. A critical point in the joint DOS appears well below the barrier bandgap energy. This

described within the picture of this QCSE. At this point the proper nature of N_2 and its different field dependence is not obvious. Fact, however, is, that we here observe an electric field controlled splitting of levels within the quantum well [15]. The merging of N_2 and N_3 then corresponds to an effectively vanishing field inside the well in agreement with findings by Takeuchi *et al.* [6]. This point of merging is achieved at finite reverse bias of ≈ -8 V and this is clear evidence of a finite electric field for open terminal conditions. Beyond the fields induced by doping in the pn-junction this is proof of finite piezoelectric field acting in the strained well. From the polarity of the diffusion field and the applied voltages we confirm the assignment of the direction of the piezo field to point from growth surface to the substrate for this biaxially compressed GaInN/GaN structure.

localization correlates with the electric field and appears to follow the well width. We therefore propose that this level indicates the effective heterostructure band offset across the strained GaInN layers. In electroreflection we confirm that levels in the well are controlled by electric fields. We confirm results of the quantum confined Stark effect in PL and observe a field dependent splitting of two levels in the well. A similar splitting arises as a function of composition. For the highest composition case, where the largest fields are identified, we observe four evenly separated levels in PR. Comparing PR and PL we find a direct correspondence of the levels, most notably a close correspondence of PR signal close to the PL evidencing the existence of a discrete level at the energy of luminescence.

ACKNOWLEDGMENT

This work was partly supported by the Ministry of Education, Science, Sports and Culture of Japan (contract nos. 09450133 and 09875083, and High-Tech Research Center Project) and JSPS Research for the Future Program in the Area of Atomic Scale Surface and Interface Dynamics under the project of Dynamic Process and Control of Buffer Layer at the Interface in Highly-Mismatched Systems.

REFERENCES

- 1 T. Takeuchi, H. Takeuchi, S. Sota, H. Sakai, H. Amano, and I. Akasaki, Jpn. J. Appl. Phys. **36**, L177 (1997).
- 2 I. Akasaki and H. Amano, Jpn. J. Appl. Phys. **36**, 5393 (1997).
- 3 C. Wetzel, H. Amano, I. Akasaki, T. Suski, J.W. Ager, E.R. Weber, E.E. Haller, and B.K. Meyer, Nitride Semiconductors, Proc. Mater. Res. Soc. **482**, 489 (1998).
- 4 C. Wetzel, T. Takeuchi, S. Yamaguchi, H. Katoh, H. Amano, and I. Akasaki, Appl. Phys. Lett. **73**, 1994 (1998).
- 5 C. Wetzel, S. Nitta, T. Takeuchi, S. Yamaguchi, H. Amano, and I. Akasaki, MRS Internet J. Nitride Semicond. Res. **3**, 31 (1998). No warranty!
<http://nsr.mij.mrs.org/3/31/Default.html>
- 6 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).
- 7 A. Hangleiter, J.S. Im, H. Kollmer, S. Heppel, J. Off, F. Scholz, MRS Internet J. Nitride Semicond. Res. **3**, 15 (1998).
- 8 A.D. Bykhovski, V.V. Kaminski, S. Shur, Q.C. Chen, and M.A. Khan, Appl. Phys. Lett. **68**, 818 (1996).
- 9 F. Bernardini, V. Fiorentini, and D. Vanderbilt, Phys. Rev. Lett. **79**, 3958 (1997).
- 10 S. Shur in Compound Semiconductors Spring I (1998) p.12
- 11 S. Chichibua, T. Azuhata, T. Sota, and S. Nakamura, Appl. Phys. Lett. **69**, 4188 (1996).
- 12 R. Denecke, J. Morais, C. Wetzel, J. Liesegang, E.E. Haller, C.S. Fadley, Proc. Mater. Res. Soc. **468**, 263 (1997).
- 13 D.E. Aspnes, Phys. Rev. B **10**, 4228 (1974); Phys. Rev. **153**, 972 (1967).
- 14 C. Wetzel, T. Takeuchi, S. Yamaguchi, H. Katoh, H. Amano, and I. Akasaki, Proc. 2nd Int. Symp. Blue Laser & Light Emitting Diodes, Kisarazu, Chiba, Japan, 1998. p.646-9.
- 15 C. Wetzel, T. Takeuchi, H. Kato, H. Amano, and I. Akasaki, Proc. 24th Int. Conf. on the Physics of Semiconductors, Jerusalem, Israel, August 2-8, 1998. *in print*.