Electric-field strength, polarization dipole, and multi-interface band offset in piezoelectric $Ga_{1-x}In_xN/GaN$ quantum-well structures

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The piezoelectric properties of $Ga_{1-x}In_xN/GaN$ multiple quantum well structures are analyzed in two sets of samples covering the composition range of $0<x<0.2$ and well widths 23 Å$\leqslant L_z \leqslant$130 Å. In photoreflection spectroscopy we observe Franz-Keldysh oscillations near the barrier band-gap energy and directly derive huge electric field values in the range of 0.23–0.90 MV/cm. The field scales with composition and strain. The onset of Franz-Keldysh oscillations marks a three-dimensional critical point that tunes with the electric field and well width. It is found to correspond to a direct interband transition between continuum states controlled in energy by the polarization dipole, i.e., the product of the polarization field and well width. By variation of the composition alone the level can be tuned over a large energy range from 3.15 to 3.37 eV. This correspondence provides a direct means to accurately determine the properties of such polarization controlled systems.

I. INTRODUCTION

The emergence of high-quality heterostructures[1,2] of wurtzite group-III nitride semiconductors reveals new means of electronic band-structure control. The uniaxial nature of this compound system together with partly ionic bonding conditions give rise to large polarization and piezoelectric effects[3,4] in thin-film heterostructures typically grown along the unique *c*-axis *z*. From an observation of the quantum confined Stark effect in the bias voltage dependence of the luminescence in $Ga_{1-x}In_xN/GaN$ quantum wells (QW's) we recently concluded the presence of very large electric fields within the pseudomorphically strained well layers.[5] In thin strained $Ga_{1-x}In_xN/GaN$ films we moreover identified Franz-Keldysh oscillations[6] (FKO's) and directly determined field strengths up to 1.1 MV/cm ($x=0.18$).[7] FKO's have also been identified in $Al_yGa_{1-y}N/GaN$ layers.[8] These large field values should also reflect in the electronic level scheme of the QW heterostructures. Here, we report the observation of a three dimensional critical point in the joint density of states (DOS) which is controlled in energy over a wide range of 225 meV by means of piezoelectric heterostructure design.[9] We employ photoreflectance (PR) spectroscopy on a large set of $Ga_{1-x}In_xN$ multiple quantum well (MQW) structures with variable composition *x* and variable well width L_z. We derive field values in the QW's and determine the multi interface bandoffsets and the associated piezoelectric dipoles.

II. EXPERIMENT

A set of nine pseudomorphic $Ga_{1-x}In_xN/GaN$ MQW structures $A, B, \ldots I$ with variable composition was grown by metal organic vapor phase epitaxy on (0001) sapphire using the technique of low-temperature deposited AlN buffer layers.[5,10] On top of a 2-μm GaN epilayer five sequences of $L_z=30$-Å $Ga_{1-x}In_xN$ QW's embedded in $L_b=60$-Å GaN barriers were grown with *x* in the range of $0<x<0.2$. From a dynamical x-ray rocking analysis the composition of three samples was determined to be $x=0.12$ (sample *E*), 0.15 (*F*), and 0.18 (*H*).[1] A second set of four $Ga_{1-x}In_xN/GaN$ MQW samples with variable well width was grown using a similar growth process and low-temperature deposited GaN buffer layers. On top of a 2-μm GaN epilayer $n=\{9,6,5,3\}$ sequences of $L_z=\{23,34,47,70\}$ Å $Ga_{1-x}In_xN$ QW's of composition $x=\{0.13,0.13,0.13,0.11\}$ were embedded in $L_b=2L_z$ GaN barriers, respectively. A further control structure of 4 wells with $L_z=L_b=130$ Å, $x=0.06$ was grown in a process similar to the latter. For all samples the well and barrier regions are undoped at residual donor concentrations of about 10^{17} cm^{-3}.

Excellent compositional homogeneity of the material on the length scale $1\leqslant r\leqslant 50$ μm was assessed by spatially resolved micro photoluminescence (PL) at excitation power densities of 1 mW/μm^2.[7] The full width of half maximum variation of the peak energy was typically $\leqslant$20 meV. PR was measured using a Xe white light source and above barrier band gap excitation by an 325 nm, 40 mW HeCd laser for photomodulation. A mechanical chopper at 1.4 kHz and lock-in technique was employed for the detection. To form the PR signal the ac component was normalized to the dc part. Due to the excitation geometry thickness interference fringes did not occur in the ac part nor in the dc part.[6] All experiments were performed at room temperature.

III. COMPOSITION DEPENDENCE

PR spectra over a selected energy range of the full composition set are presented in Fig. 1. Spectra are arranged in the sequence of the PL peak energy (see labels in Fig. 1)[11] which is a measure also for the composition *x* and the in-

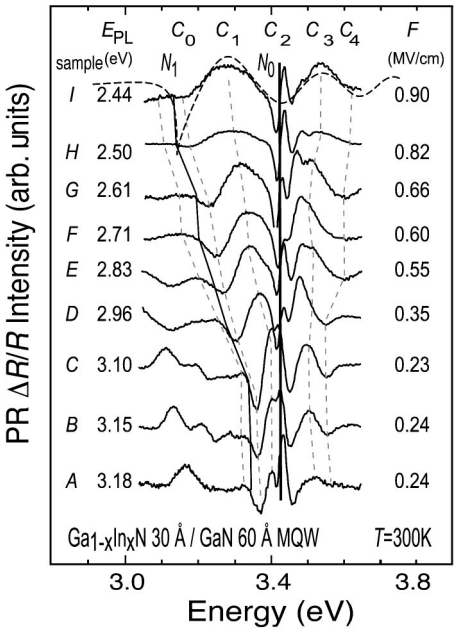

FIG. 1. Photoreflection spectra of $Ga_{1-x}In_xN$/GaN MQW structures for variable x and fixed well width presented in the sequence of PL peak energy (labels). The excitonic barrier-band-gap energy appears as a narrow oscillation (N_0). Superimposed is a wider oscillation with extrema in C_i, $i=0\ldots4$. They are assigned to Franz-Keldysh oscillations in the presence of a large electric field F and define a three dimensional critical point in N_1. The scaled electro-optical function $G(\eta)$ is given as a fit to one spectrum (dashed line). Field values derived from the FKO interpretation are indicated.

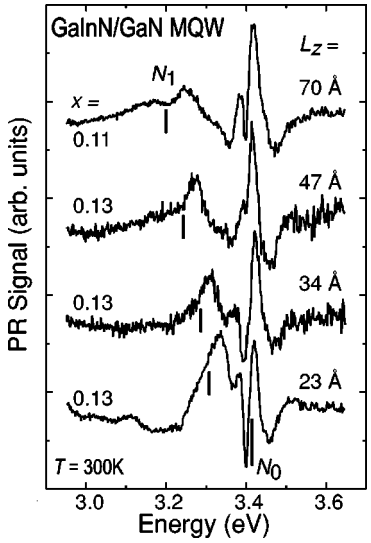

FIG. 2. Photoreflection in the sample series with variable well width and similar composition. The levels of N_0 and N_1 are indicated. The splitting increases with the well width L_z. FKO's can not be identified due to strong excitonic contributions at the GaN barrier bandedge.

plane strain ϵ_{xx}.[10] Several PR contributions can be identified. At 3.425 eV (N_0) narrow oscillations are seen that closely correspond to the excitonic band gap in the GaN epilayer. PR in GaN epilayers has been shown to reflect the wurtzite structure and its three associated excitons A,B, and C.[12] Within the typical strain of epitaxial GaN excitonic level splitting of A and B accounts for up to 8 meV and has been shown to produce a structure very similar to the signal seen here. The higher-lying C exciton is usually difficult to detect and not identified in our spectra. Such excitonic features have been described by the superposition of third derivative-like structures.[13] Within the context of this paper features of this fine detail are presently not of concern and we jointly assign N_0 to the excitonic band gap E_{gX} some 20 – 30 meV below the fundamental GaN band gap. Within a broader energy range around N_0, a strong periodic modulation of the PR signal with several minima and maxima labeled C_i,$i=0\ldots4$ is seen in all these samples. Comparing the entire sample set, a trend towards wider oscillation period for higher x appears. Extrema C_i appear independently of the oscillations in N_0 indicating that the resulting PR signal is a superposition of both oscillations. The lowest minimum C_0 is accompanied by a weak positive contribution on the lower energy side and marks a clear onset of the oscillations in N_1.

IV. WELL WIDTH DEPENDENCE

More conclusive information is obtained from the second sample set with variable well width (Fig. 2). Here very strong PR oscillations N_0 at the excitonic band gap are identified. The onset point N_1 is also identified as indicated in Fig. 2. In contrast to the composition set samples, however, further extrema associated with periodic oscillations can not be identified due to the strong excitonic contributions in N_0. This is tentatively associated to an improved material quality in the GaN epilayer in this more recently grown well width sample set. Here the splitting of N_0 and N_1 is found to increase with the well width. On the other hand, excitonic features are very weak in the control sample [Fig. 3(a)]. Here several well pronounced oscillations with extrema in C_i appear above an onset in N_1 at 3.315 eV. Only a weak perturbation is seen by the excitonic band gap in N_0 here at 3.40 eV. The variations in the level of N_0 is associated with the different buffer layer technique employed.

V. DISCUSSION

The oscillations with extrema in C_i in the composition sample set strongly resemble FKO's near a three dimensional critical point in the joint DOS. Such oscillations appear when carriers free to move in one direction $\vec{r}$ are subject to a large electric field along the same direction. This can be the case in bulk crystals and in two-dimensional structures for in-plane electric fields (two-dimensional critical point). This can also be the case in QW structures for fields along the growth direction for resonant states above the wells. From the oscillation behavior the electric field strength F can be determined very directly. In this the effective joint DOS mass μ along $\vec{r}$ is the only material related parameter. The critical point corresponds to N_1 in our data and appears with an apparent localization energy $\Delta_{01}=E(N_0)-E(N_1)$ with respect to the excitonic barrier band-gap energy. FKO's can be well described in theory[14] by the electro optical functions $F(\eta)$ and $G(\eta)$ where η is a reduced energy scale $\eta=(E-E_0)/(\hbar\Theta)$, where in turn E_0 is the energy of the critical

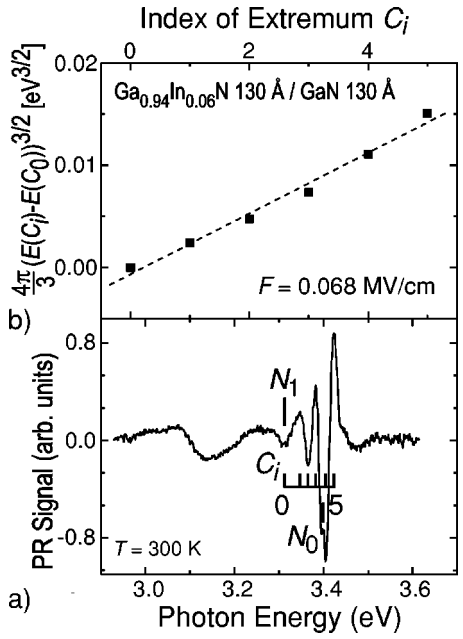

FIG. 3. (a) Photoreflection of a control sample with wider well and a similar barrier width. The limited intensity of excitonic signal at the GaN barrier band gap energy (N_0) reveal clear extrema of the FKO's. The presence of several extrema between N_0 and N_1 contradicts the assumption of FKO's to occur within the barrier region. (b) The interpretation of FKO extrema reveal a good fit of the model. (For details see text.)

point and $\hbar\Theta$ is the electro optical energy.[15,16] $\hbar\Theta$ is related to the electric field $F=(\hbar\Theta)^{3/2}\sqrt{2\mu}/e\hbar$. In this, $\mu=0.2m_0$ is the reduced effective mass assumed at the electron effective mass value of GaN due to the lack of further data.[17] In Fig. 1, $G(\eta)$ is shown together with the spectrum of sample *I*. A clear correspondence in all the features, namely a weaker extremum at lowest energy, a dominant minimum in C_0, and subsidiary extrema in C_1, C_2, C_3, and C_4 are clearly recognized.

As proposed by Aspnes,[14] the energy separation of the extrema can be used to determine $\hbar\Theta$ and F. Within a commonly used approximation of cosine functions a plot of $4/3\pi\times[E(C_i)-E(C_0)]^{3/2}$ versus the indices of the extrema i is shown in Fig. 4. For each sample extrema can be well approximated by straight lines the slope of which corresponds to $(\hbar\Theta)^{3/2}$. Note that similarly to the higher extrema, $E(C_0)$ is also subject to error bars and therefore not a fixed point of the approximating line. Very large values of the electric field in the range of $F=0.23$ MV/cm to 0.90 MV/cm are thus derived and the field increases in the sequences of decreasing PL energy, i.e., increasing composition x and/or strain ϵ_{xx}. An alternate interpretation by fitting $G(\eta)$ to the PR spectra achieves identical values to within $\pm 5\%$.

A clear distinction of FKO's and excitonic features is not possible in all samples. However, within the control sample contributions of the N_0 transition are rather weak allowing a clear assignment of FKOs (Fig. 3). Several oscillations extrema separate N_0 and N_1 in energy. Due to the small impact of the N_0 level in the spectrum of this sample FKO's are very well resolved leading to an accurate reading of the electric field $F=0.068$ MV/cm.

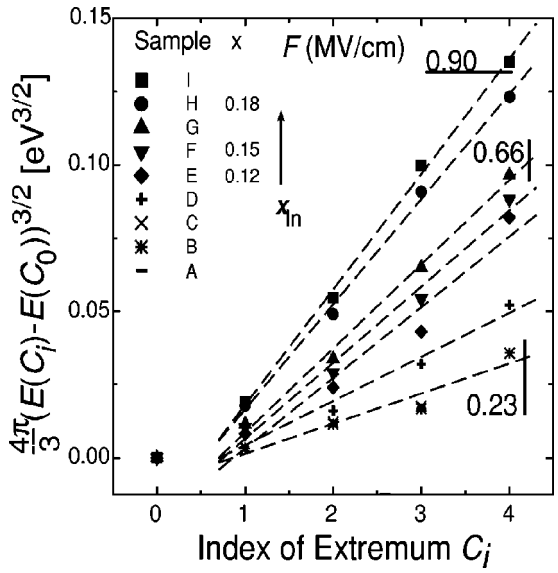

FIG. 4. Interpretation of the oscillation extrema versus their index i in terms of FKO's within the composition series. Points can be well approximated by straight lines, the slope of which corresponds to the electro-optical energy $(\hbar\Theta)^{3/2}$ and therefore to F. Very large field values increasing along x and strain up to $F=0.90$ MV/cm$\pm 10\%$ are identified.

Two factors are expected to contribute in the observed electric field.[4] First, the alloy discontinuity along z at the GaN-GaInN interface may lead to a discontinuity in polarization and induce δ charges of opposite polarity at both hetero interfaces of each well, respectively. Secondly, the discontinuity of biaxial strain by pseudomorphic growth should induce piezoelectric δ charges and act in a similar way. As shown in thin strained films the resulting electric field is proportional to the alloy composition and the associated strain.[7] According to first-principles calculations the piezoelectric effect dominates in $Ga_xIn_{1-x}N$/GaN heterostructures while the compositional polarization effect should dominate in $Al_yGa_{1-y}N$/GaN systems.[4] We consequently discuss the present system in terms of the piezoelectric effect.

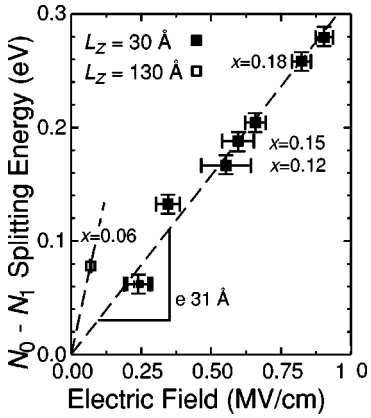

FIG. 5. Correlation of apparent localization energy Δ_{01} and the electric field as derived from the FKO's. Within the composition set a linear correspondence $\Delta_{01}=FeL_{\text{eff}}$ with a slope parameter $L_{\text{eff}}\approx L_z$ is found. This indicates that the critical point N_1 is controlled by the piezoelectric dipole defined by the structure of the quantum well.

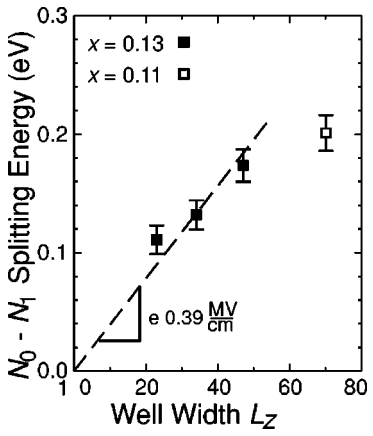

FIG. 6. Correlation of apparent localization energy Δ_{01} and the well width within one growth process. A straight line through the origin $\Delta_{01}=F_{\mathrm{eff}}eL_z$ can well describe the samples of $x=0.13$.

The occurrence of a three-dimensional critical point N_1 *below* the barrier band-gap energy may surprise but can be explained by the following considerations. When plotting the apparent localization energy Δ_{01} in the composition samples versus the determined electric field values (Fig. 5) we observe a linear correlation according to $\Delta_{01}=FeL_{\mathrm{eff}}$, where $L_{\mathrm{eff}}=31$ Å, which is very close to the well width $L_z=30$ Å. In turn the interpretation of the well width dependence reveals a similar picture (Fig. 6). For $x=0.13$ the splitting can be well approximated by $\Delta_{01}=F_{\mathrm{eff}}eL_z$ with a very reasonable field strength of $F_{\mathrm{eff}}=0.39$ MV/cm. The value for $x=0.11$ deviates somewhat to a lower field value. This complete test for both dependencies on L_z and F indeed suggest a relation of the form:

$$\Delta_{01}=FeL_z. \tag{1}$$

Most notably the splitting is expected to vanish in the limit of absence of the well. Application of Eq. (1) to the control sample leads to $L_{\mathrm{eff}}=125$ Å in excellent agreement with the well width determined in the x-ray rocking analysis $L_z=130$ Å.

VI. BAND-STRUCTURE MODEL

To resolve the origin of these relations we propose the following bandstructure scheme (Fig. 7). The polarization δ-charges P define a piezoelectric dipole across each well ($\epsilon_r=10.4$)

$$P\ L_z=\epsilon_0\epsilon_r FL_z. \tag{2}$$

This results in an effective multi interface bandoffset across the GaN-$Ga_{1-x}In_xN$-GaN sequence of $|\Delta E_c|=|\Delta E_v|=FeL_z$ for each QW in the MQW structure. Within the region of the well bound electronic states are then controlled by pairs of asymmetric barriers. The edges for free continuum states are defined by the respectively lower side for electrons and the higher side for holes within the asymmetric structure. Additional bound states in the depth of the well responsible for the PL should exist but they are not of relevance in this interpretation. Consequently a three-dimensional critical point appears and corresponds to a direct transition between both edges of the continuum states (N_1).

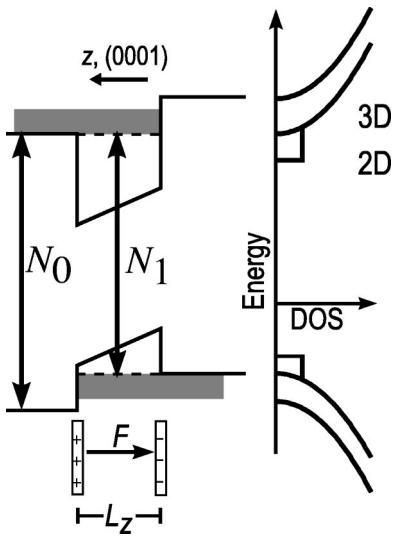

FIG. 7. Schematic of the band structure in the vicinity of the strained quantum well. An effective bandoffset FeL_z across the GaN-$Ga_{1-x}In_xN$-GaN multiple interface is defined and controlled by the piezoelectric field and the well width. Asymmetric barriers in the well give rise to a spatially direct interband transition between continuum states extending in the barriers on opposite sides of the well. Quantized levels within the well are not considered here.

Due to the asymmetric well those resonant states of holes and electrons extend into opposite half spheres of real space. It should be noted that although the field is active in the well the band edges of the continua are not tilted in real space. We assume that this may support the clear observation of the FKO's in these structures.

In response to the polarization across the wells a field within the barriers of the order of FL_z/L_b is expected to align the Fermi level at both ends of the structure. The appearance of several extrema $C_i, i\geqslant 0$, between N_0 and N_1, i.e., in the control sample (Fig. 3), however, clearly rules out an origin of the observed FKO's within the GaN barrier.

The proposed transition has a large overlapp of the wavefunctions for electrons and holes and does not require any tunneling in real space. Its energy is entirely controlled by the barrier band-gap energy, the well width, and the piezoelectric, or more generally, the polarization properties of the heterostructure: $E(N_1)=E(N_0)-FeL_z$. It is independent of the precise DOS within the well. In our set of samples $E(N_1)$ can be varied within a large range of 225 meV between 3.15 and 3.37 eV. The very close correspondence of the electric field and the apparent localization derived in the composition and well width dependencies therefore strongly supports our interpretation of the FKO's. In the limit of large well width and large field our model for N_1 merges with the interpretation of long-lived luminescence in GaN/$Al_yGa_{1-y}N$ quantum wells.[18]

VII. CONCLUSIONS

In summary, we have presented an analysis of photoreflection spectra in a large set of $Ga_{1-x}In_xN$/GaN multiple quantum well structures covering the relevant composition range of $0<x<0.2$ and the relevant well width range 23 Å$\leqslant L_z\leqslant$130 Å. Interpreting Franz-Keldysh oscillations

we directly determine huge electric fields acting within the wells. We find a direct correspondence with the occurrence of a three-dimensional critical point in the spectra, which allows for an accurate determination and correlation of the crucial properties of well width, electric field, reduced effective mass, composition, and strain. The critical point can be varied in energy over a large range by the structural properties of the hetero interface. We associate the corresponding level to a direct transition between continuum states in the quantum well with asymmetric barriers controlled by an effective band offset across the GaN-$Ga_{1-x}In_xN$-GaN multiple interface of $|\Delta E_c| = |\Delta E_v| = FeL_z$. This allows for an accurate determination of either parameter out of μ, F, L_z, x, and ϵ_r. This fact should be most beneficial for the accurate description of the electronic band structure within polarization heterostructures in general and the quantized levels in $Al_yGa_{1-x-y}In_xN$ heterostructures in particular.

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