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The role of piezoelectric fields in GaN-based quantum wells

Andreas Hangleiter [1], Jin Seo Im[1], H. Kollmer[1], S. Heppel[1], J. Off[1] and Ferdinand Scholz[1]
[1]*4. Physikalisches Institut, Universität Stuttgart,*

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In this contribution, we focus on the consequences of the piezoelectric field, which is an inherent consequence of the commonly used wurtzite phase of GaN, on the optical properties of strained GaN-based quantum well structures. We demonstrate that both in GaN/AlGaN and in GaInN/GaN single quantum well structures, the piezoelectric field leads to a Stark-shift of the fundamental optical transitions, which can lead to luminescence emission far below the bulk bandgap. Due to the spatial separation of the electron and hole wavefunctions in such structures, the oscillator strength of these transitions may become extremely small, many orders of magnitude lower than in the field-free case. From specially designed structures, we can even determine the sign of the piezoelectric field and relate it to the polarity of the layers. Under high-excitation conditions, as found in a laser diode, the piezoelectric field is almost completely screened by the injected carriers. As a consequence, the stimulated emission is significantly blue-shifted compared to the photoluminescence, which has sometimes been confused with localization effects.

1 Introduction

GaInN/GaN/AlGaN quantum well structures are now at the heart of GaN-based LED‘s and lasers, which are commercially available or soon to be commercialized [1] [2]. Nevertheless, the fundamental mechanisms of spontaneous and stimulated light emission are still subject to quite some debate. In particular, localization effects due to composition fluctuations and even quantum-dot-like structures due to phase separation in GaInN quantum wells have been invoked to explain some of the observations [3] [4].

Even more recently, it has been pointed out that many of the unusual optical properties of GaN-based heterostructures can be consistently explained by considering the piezoelectric properties of the III-nitrides [5] [6]. In fact, the importance of piezoelectric fields in III-V semiconductors has first been recognized for cubic zincblende heterostructures grown on a (111) plane [7]. The characteristics of such structures and some novel device applications have been discussed in detail [8] [9] [10]. On the other hand, AlN has long been known as a strongly piezoelectric, though insulating material. For the semiconducting III-nitrides, piezoelectric effects have first been discussed in the context of heterostructure field effect transistors [11] [12]. In such devices, the piezoelectric fields lead to a significant change of device characteristics and to new optimization strategies.

In this paper, we discuss the consequences of piezoelectric fields on the optical properties of GaN-based heterostructures and quantum wells. We demonstrate that the piezoelectric fields lead to a strong red-shift of the luminescence with respect to the bulk bandgap and the absorption edge, and to a dramatically reduced oscillator strength. Using specially designed test structures we determine the sign of the field and discuss its relation with the crystal orientation. We compare the photoluminescence with the stimulated emission and highlight the effects of screening of the piezoelectric field.

2 Piezoelectric fields

Non-centrosymmetric crystals, when subject to external stress, may generate so-called piezoelectric fields due to a stress-induced polarization. The electric polarization field is given by

$$P_i = d_{ik}\,\sigma_k \quad (i=x,y,z;\ k=xx,yy,zz,yz,zx,xy) \qquad (1)$$

where P_i is the electric polarization field, d_{ik} is the piezoelectric tensor, and σ_k is the *stress* tensor. We note that the polarization may also be related to the *strain* tensor ε_k by another piezoelectric tensor denoted by e_{ik}.

In the wurtzite structure typically occuring for the III-nitrides, biaxial strain in the (0001) plane results in a polarization field, which is most conveniently expressed by [13]

$$P_z = 2d_{31}(c_{11} + c_{12} - \frac{2c_{13}^2}{c_{33}})\epsilon_{xx}, \tag{2}$$

where d_{31} is the piezoelectric constant, c_{ij} are the elastic constants, and ε_{xx} is the in-plane strain. Such a coherent in-plane strain is realized in case of pseudomorphically grown heterostructures with dissimilar lattice constants. The sign of the polarization of course depends on whether the strain is compressive or tensile.

3 Experimental

Our samples were grown on 0001-oriented sapphire substrates using low pressure metal-organic vapor phase epitaxy (LP-MOVPE) and employing an AlN nucleation layer. The GaInN layers were grown at temperatures at or below 800 °C with N_2 as a carrier gas. GaInN/GaN, GaN/AlGaN, and GaN/GaInN/AlGaN double heterostructures (DH) as well as single quantum wells (SQW's) of different thicknesses were investigated. The GaInN/GaN structures consisted of a 500 nm to 2 µm thick GaN buffer, a GaInN quantum well with varying In content, and a 50 nm GaN cap layer, whereas the GaN/AlGaN structures had a 500 nm AlGaN (≈15 % Al) buffer, a GaN well, and a 50 nm AlGaN cap layer.

Time-resolved spectroscopy with resonant excitation of the quantum wells was performed using a setup already described elsewhere [14]. The stimulated emission of the samples under high excitation conditions was studied utilizing the stripe excitation method as described earlier [15].

4 Oscillator strength in GaN/AlGaN and GaInN/GaN quantum wells

4.1 Basic observations

First, we have studied GaN/AlGaN and GaInN/GaN single quantum wells (SQW's) with varying well thickness. For the GaN/AlGaN quantum wells, for example, time-integrated low-temperature luminescence spectra exhibited a fairly complex behavior. Besides the AlGaN emission at 3.75 eV, we observe two emission lines from thick quantum wells but only a single line from thin QW's. As shown in Figure 1, thin quantum wells (1 nm and 2 nm) show a clear blue-shift of their emission due to size quantization. In thicker layers (5 nm and 10 nm) the higher energy emission line is about 70 meV above the GaN bandgap, whereas the lower energy line shifts to energies well below the GaN bandgap with increasing thickness.

Measurements of the luminescence decay time (Figure 2) reveal that both the single line in thin QW's as well as the higher energy line in thicker layers have decay times of about 300 ps. The lower energy line in the thicker layers becomes extremely slow for the 10 nm sample, with a decay time of 3 µs. Time-resolved spectra of the lower energy line show that there is a red-shift of the emission peak of 27 meV for long delay times after pulsed excitation.

A very similar behavior was observed for several sets of GaInN/GaN QW's, with the decay time of the lower energy line gradually increasing into the microsecond range with increasing well thickness.

4.2 Discussion and model

Basically, there are three possible explanations for the origin of the low-energy emission line found both in GaN/AlGaN and in GaInN/GaN structures.

1. In GaInN/GaN MQW structures a red-shifting emission has already been attributed to localized excitons or quantum dots.
2. The extremely slow luminescence decay could be an indication for spatially indirect donor-acceptor-like transitions.
3. Piezoelectric fields due to mismatch-induced strain could lead to a Stark-shift of the emission and to a strong reduction of the oscillator strength.

Donor-acceptor-like impurity-related transitions can be excluded since it is hard to see how such transitions would shift to lower energy with increasing well width. Localization or quantum dots can not be the origin of this behavior for two reasons: i) for the GaN/AlGaN samples such transitions could not be below the bulk GaN bandgap; ii) the extremely slow decay in thick layers would require a localization to a radius of less than 1 Angstrom, which is clearly not feasible.

Let us now explore the case of piezoelectric fields in some detail. We have to recall that our sample design is such that the active quantum well is strained whereas the barriers are unstrained both for the GaInN/GaN and for the GaN/AlGaN structures. A qualitative picture with the energies and wavefunctions involved is shown in Figure 3. Due to the piezoelectric field, the energy levels of the quantum wells are red-shifted with increasing well width. At the same time, the electron and the hole wavefunction are more and more separated leading to a dramatic reduction in oscillator strength. We have performed a quantitative numerical calculation of the quantization energies, wavefunctions, and matrix elements for such a situation.

A comparison of the calculated energies and oscillator strengths with the experimental data is shown in Figure 4 for GaN/AlGaN QW's. For this figure, the energetic positions were taken from spectra at the long-

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est possible delay time after excitation, i.e. with screening of the field being as small as possible. The calculated curves include only a single adjustable parameter (the band discontinuities were taken from the literature [16]), which is the magnitude of the piezoelectric field. In the present case, a field of 350 kV/cm consistently explains both the red-shift and the dramatic increase of the decay time with increasing well width.

Moreover, Figure 4 also explains the origin of the higher energy line in the thick layers: It is due to spatially direct transitions in the strained GaN well layer. The dashed-dotted line was calculated on the basis of the known strain of about 0.4 % of the GaN layer and coincides almost perfectly with the measured position of the corresponding luminescence peaks.

Figure 5 summarizes our results for a series of GaInN/GaN single quantum wells. In this case, the analysis of the emission peaks yields a piezoelectric field of about 300 kV/cm. From x-ray diffraction data we estimate the strain to be of the order 0.3 %. Unlike the case of the GaN/AlGaN structures, the calculation of the decay times does not fit the experimental value for the largest well width. As we will show later on, this is related to the small conduction band discontinuity in the GaInN/GaN system, which leads to a rather weak electron confinement in such quantum wells.

5 Carrier confinement and sign of the piezoelectric field

5.1 Results for asymmetric test samples

In order to study the effects of carrier confinement on piezoelectric field effects in nitride quantum wells in more detail, we have designed and fabricated a set of samples with asymmetric barriers, as shown in Figure 6a. Besides a control sample with a 7 nm GaInN quantum well sandwiched between GaN barriers, these samples had a 20 nm AlGaN barrier either ”below“ or ”above“ the quantum well.

The results of time-resolved photoluminescence measurements are shown in Figure 7. Very clearly, the luminescence decay is much faster (by almost 3 orders of magnitude) for the sample with the AlGaN barrier on top of the quantum well than for the one with the AlGaN barrier below the quantum well. In other words, the oscillator strength is much larger for the former sample than for the latter one. This indicates that carriers are much better confined in the first sample.

These results are compared to those obtained for samples with simple GaN barriers in Figure 8. One can see that the result for the control sample is in line with the data for the thickness series discussed earlier. On the other hand, the decay time is larger for the sample with the bottom AlGaN barrier, whereas it is smaller for the sample with the top AlGaN barrier. Interestingly, the latter result fits well with our calculation for the well width dependence of the decay time.

5.2 Carrier confinement and sign of the field

The origin of the different behavior of the asymmetric samples is explained in Figure 9 and Figure 10. Since the piezoelectric field introduces a natural asymmetry into the structures, it makes a big difference whether the AlGaN barrier is below or on top of the quantum well, depending on the direction of the piezoelectric field. In the latter case (Figure 10), if the field points towards the substrate, electrons are strongly confined by the large GaInN/AlGaN heterobarrier towards the top surface. In the former case (Figure 9), electrons are confined only by the small GaInN/GaN heterobarrier. Since the oscillator strength is directly related to the overlap of the electron and hole wavefunctions, the observed difference between the asymmetric samples is clearly related to the piezoelectric field.

Moreover, if the piezoelectric field had the opposite sign, the difference between the samples should be the other way round, i.e. the sample with the top AlGaN barrier should exhibit are smaller oscillator strength. Therefore, our results allow for an unambiguous determination of the sign of the piezoelectric field, which is shown to point towards the substrate.

5.3 Polarity of the layers and piezoelectric coefficient

It is interesting to discuss this result in the context of the polarity of the nitride layers. From hemispherically scanned x-ray photoelectron diffraction (HSXPD) and other data [17], it seems to be well established that good MOVPE samples with smooth surfaces, grown on c-plane sapphire, are Ga-face, i.e. have a single Ga-N bond pointing towards the surface. On the other hand, theoretical calculations by Bernardini *et al.* [18] predict a negative sign of the piezoelectric coefficient d_{31}. In fact, our result is consistent with this prediction, assuming that our samples are Ga-face.

The piezoelectric coefficient derived from our data according to Equation (2) and using the elastic constants from Ref. [19] is $d_{31} \approx -0.9 \times 10^{-10}$ cm/V, both for the GaN/AlGaN and for the GaInN/GaN structures. Since the In content in the GaInN/GaN samples discussed here was low, we have used the GaN elastic constants for the GaInN as well.

6 High excitation, optical gain, and screening effects

Under strong pumping conditions, such as in a semiconductor laser, the quantum wells become populated with

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charge carriers, which screen the piezoelectric field. This becomes evident, for example, when looking at time-resolved photoluminescence spectra of quantum wells. As shown in Figure 11 for the sample with an AlGaN barrier below the quantum well, the luminescence peak shifts to lower energy by about 230 meV from immediately after the excitation pulse towards long delay times. This is due to the fact that the carrier population created by the excitation pulse decays, thus reducing the screening charge and increasing the effective field towards its equilibrium value.

Under even higher excitation, as necessary to achieve inversion and optical gain the field becomes almost completely screened. In Figure 12 we compare the low-temperature photoluminescence spectra (pump power ≈ W/cm^2) and room-temperature stimulated emission spectra (pump power ≈ MW/cm^2) of GaInN/GaN quantum wells of different thicknesses, but almost identical In mole fraction. We note that there is a large energy shift of 150 meV and 290 meV, respectively, between the low-excitation photoluminescence peak and the high-excitation stimulated emission peak. The size of this energy shift strongly depends on well width, which confirms its origin as being due to the piezoelectric field. Moreover, the position of the stimulated emission peak does no longer depend significantly on pump power, which indicates that the field is almost completely screened under these conditions. The position of the stimulated emission peak is therefore a good measure of the real bandgap energy of the GaInN quantum well, without any Stark-shift.

7 Discussion

Piezoelectric fields are now emerging as a dominant factor for the optical and electrical properties of nitride heterostructures. In fact, most of the observations previously attributed to localization effects [3] [4] can be easily explained:

1. The large Stokes shift between emission and absorption in GaInN/GaN (and GaN/AlGaN) quantum wells is due to the fact that Stark-shifted states do dominate the luminescence, while they cannot efficiently absorb light due to their very small oscillator strength. Only highly excited states, which are close to the flatband bandgap, contribute significantly to the absorption.

2. The large and energy-dependent decay time of the photoluminescence are due to the reduced oscillator strength and to the screening-induced red-shift of the luminescence peak towards long delay times.

3. The blue-shift of the emission of quantum well LED‘s for large forward currents is due to screening of the piezoelectric field.

Moreover, there are additional issues, which can not be easily explained by localization effects:

1. The characteristic well width dependence of the peak positions and the decay times can not be accounted for by localization effects.

2. Localization effects are unable to explain the extremely long decay times, well in the microsecond range, for thick quantum wells.

3. The ”negative“ quantization energies for thick quantum wells (i.e. peak energies below the bulk bandgap), which are obvious at least for GaN/AlGaN quantum wells are not possible without piezoelectric fields.

Of course, there may still be localization of carriers due to well width fluctuations, composition fluctuations, or even phase separation of GaN and InN. The dominant effect, however, for the optical and electrical properties of nitride heterostructures appears to the piezoelectric fields rather than any localization effect.

8 Conclusion

In conclusion, we have shown that the optical properties of GaInN/GaN and GaN/AlGaN quantum wells are dominated by effects of the piezoelectric field due to the elastic strain built into these layers. Both the oscillator strength and the effective bandgap exhibit a characteristic well-width dependence. Compared to the piezoelectric effects, localization of carriers at composition fluctuations plays only a minor role. By introducing an AlGaN barrier either below or on top of a GaInN/GaN quantum well, the carrier confinement of the well can be manipulated. This allows us to determine the direction of the piezoelectric field to be towards the substrate in case of compressive in-plane strain. Under strong pumping conditions, such as in a laser diode, the piezoelectric field becomes almost completely screened.

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FIGURES

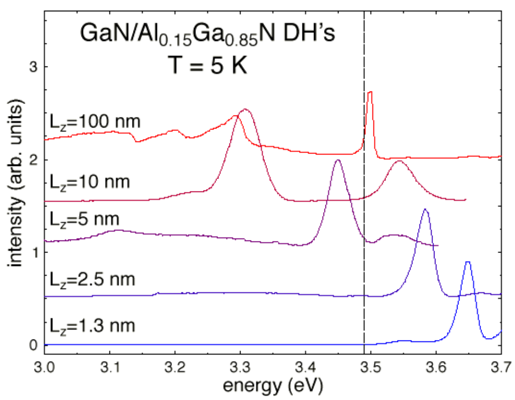

Figure 1. Time-integrated photoluminescence spectra of a series of GaN/AlGaN quantum wells. The dashed line indicates the position of the GaN bandgap.

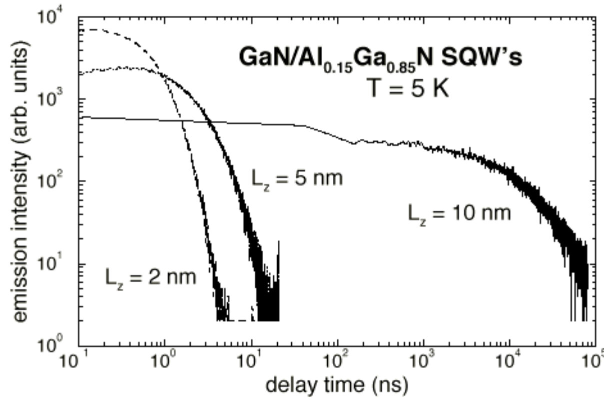

Figure 2. Double-logarithmic plot of the luminescence decay for a 2 nm, a 5 nm, and a 10 nm GaN/AlGaN quantum well. The thickest layer shows a decay on a microsecond timescale.

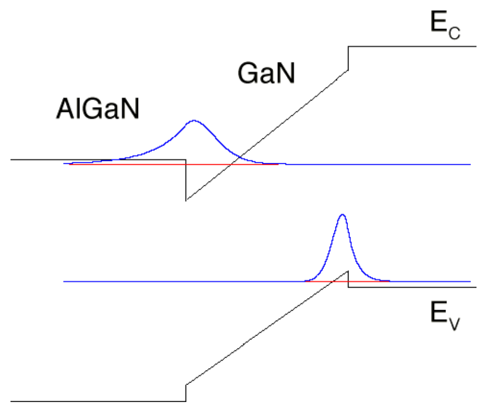

Figure 3. Schematic picture of the energies and wavefunctions of electrons and holes in a strained quantum well with a piezoelectric field.

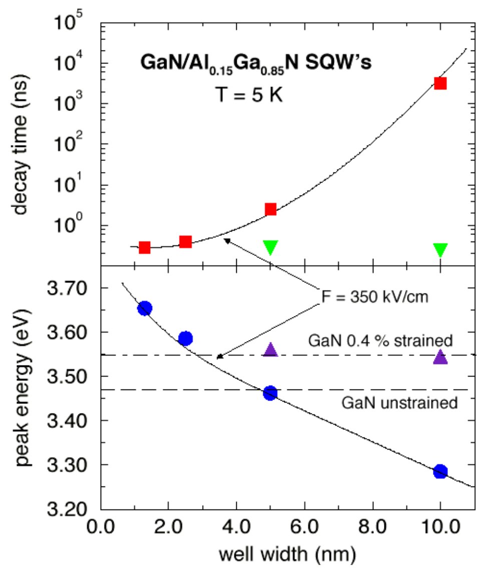

Figure 4. Comparison of the measured energy positions (dots) and decay times (squares) of the low-energy lines in GaN/ AlGaN SQW's with a calculation based on piezoelectric fields. The triangles give the values for the respective higher-energy emission lines.

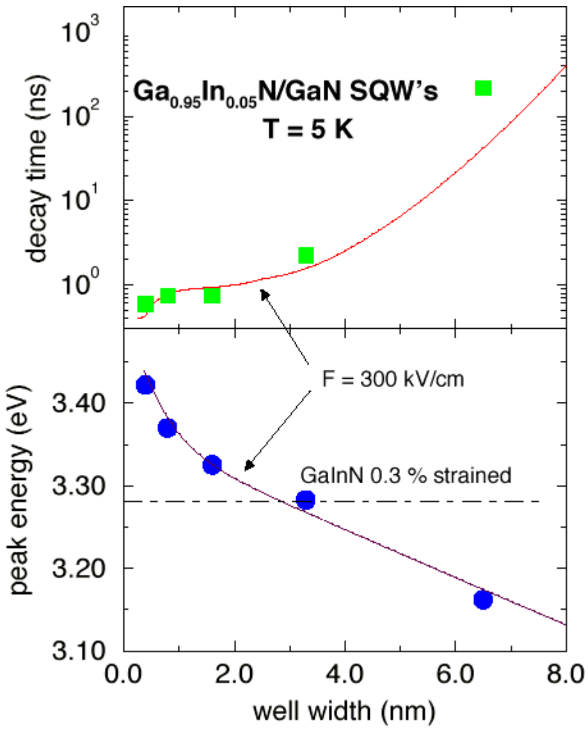

Figure 5. Comparison of the measured energy positions (dots) and decay times (squares) of the low-energy lines in GaInN/ GaN SQW's with a calculation based on piezoelectric fields.

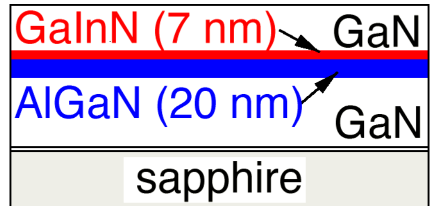

Figure 6a. Layer sequence of the asymmetric GaN/GaInN/ AlGaN test structures.

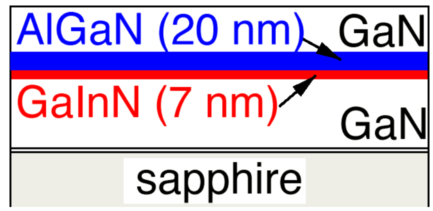

Figure 6b. Layer sequence of the asymmetric GaN/GaInN/ AlGaN test structures.

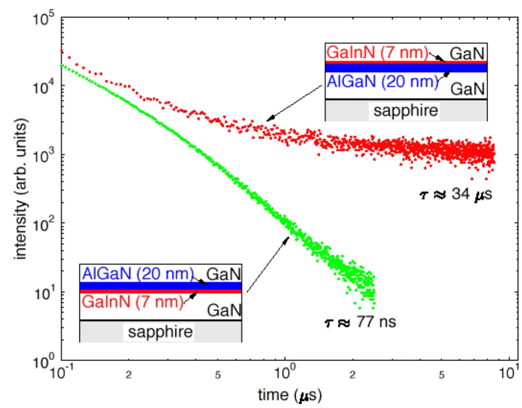

Figure 7. Comparison of the luminescence decay after pulsed excitation for the two test samples with an AlGaN barrier above or below the GaInN quantum well.

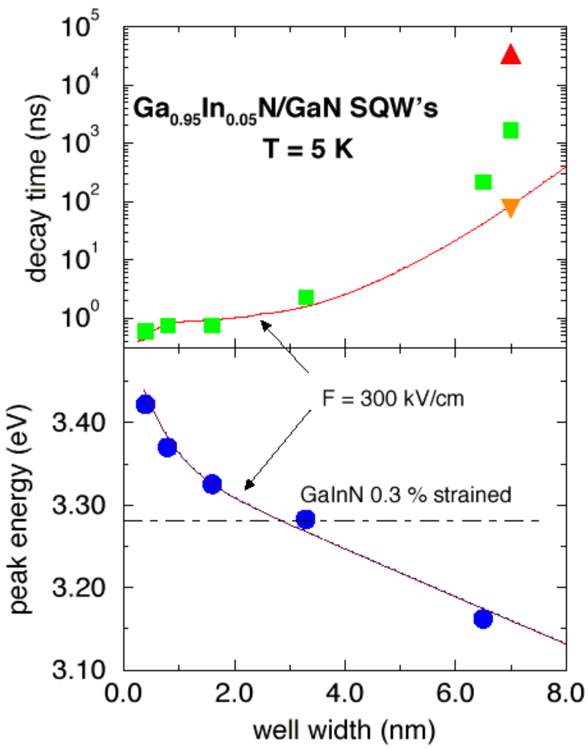

Figure 8. Comparison of the measured decay times for the test samples with those from symmetric GaInN/GaN quantum wells with the sample In mole fraction.

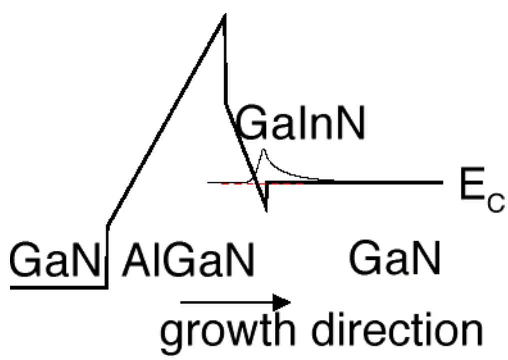

Figure 9. Schematic view of the conduction band in the sample with an AlGaN barrier below the GaInN quantum well.

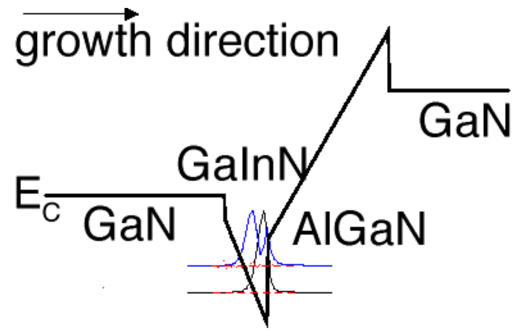

Figure 10. Schematic view of the conduction band in the sample with an AlGaN barrier on top of the GaInN quantum well.

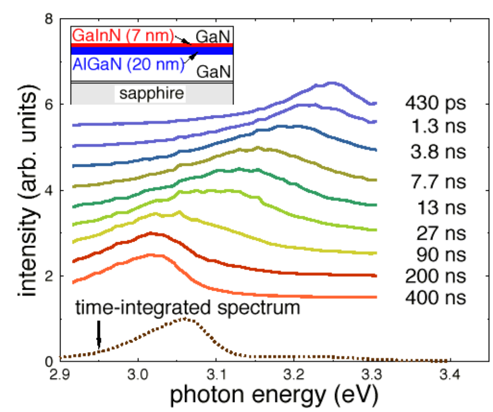

Figure 11. Time-resolved photoluminescence spectra of the GaN/GaInN/AlGaN quantum well showing the effect of screening of the piezoelectric field by photogenerated carriers.

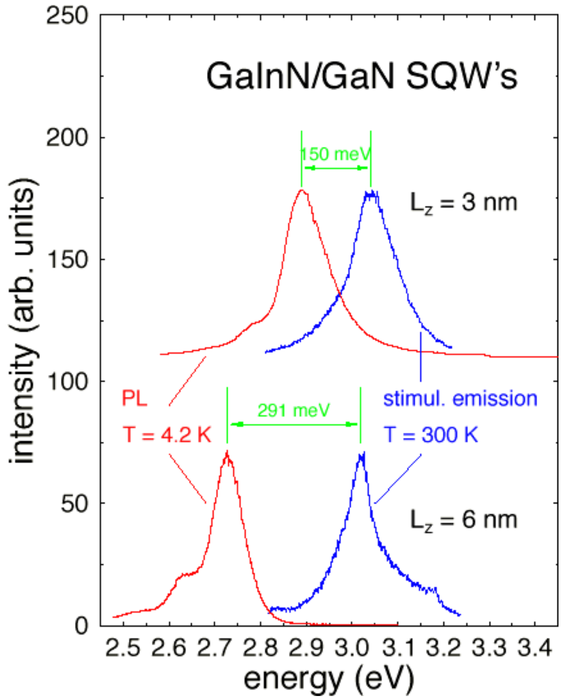

Figure 12. Photoluminescence and stimulated emission spectra of GaInN/GaN quantum wells with 3 nm and 6 nm well thickness.

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