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Photoluminescence of GaN epitaxial layers

R Dai†‡, S Fu‡, J Xie‡, G Fan‡, G Hu‡, H Schrey§ and C Klingshirn§||

‡ Changchun Institute of Physics, Changchun, China

§ Institut für Angewandte Physik der Universität Karlsruhe, D-7500 Karlsruhe, Germany

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Abstract. The characteristic photoluminescence lines in GaN undoped epitaxial layers have been investigated in a large number of samples at low temperature. The lines observed in the high-energy part of the photoluminescence spectra are called I_1, I_2, I_3 and I_4 with decreasing photon energy. I_1, situated at 3.476 ± 0.002 eV and I_4 at 3.311 ± 0.002 eV are reported here for the first time. Their dependences on temperature and excitation intensity have also been measured. These lines are proposed to be due to bound exciton emission at localised centres and to donor–acceptor pair recombination caused by imperfections and nitrogen vacancies in the crystal. The thermal activation energies are determined as $\Delta E_1 =$ 1.9 meV, $\Delta E_3 = 3.4$ meV and $\Delta E_4 = 14.4$ meV. A new value for the lowest transverse free exciton in GaN at 3.479 ± 0.002 eV is suggested.

1. Introduction

In the hope that gallium nitride may be a useful luminescent material, which can emit light over almost the whole visible region with a relatively high efficiency, several groups all over the world are investigating the growth, luminescence, electrical and other properties of this material. Though GaN belongs to the III–V compounds it is in some respects similar to the II–VI materials: it is a direct gap semiconductor, which crystallises in the wurtzite structure (point group C_{6V}) and has an energy gap of the order of 3.5 eV. GaN is often grown by vapor phase epitaxy (Maruska and Thietjen 1969), generally on sapphire substrate. Light-emitting diodes produced with GaN (Jacob and Bois 1977) have sometimes rather high efficiencies. In spite of this fact, GaN is still not yet a material for practical application. The elementary difficulty in this field is that the defects influence the electrical and luminescence properties of the crystal seriously. Therefore not only the properties of light emitting GaN diodes but even the fundamental properties of undoped crystals change from one author to another, and from sample to sample. The photoluminescence spectra e.g. of undoped GaN epitaxial layers, which were measured by Pakove *et al* (1970), Dingle *et al* (1971, 1972) and Cunnigham *et al* (1972) and others, are quite different from each other, and the broad luminescence bands give only rather poor information about the properties of the crystals.

† Present address: Institut für Angewandte Physik der Universität Karlsruhe, D-7500 Karlsruhe, Germany.

|| Present address: Physikalisches Institut der Universität, D-6000 Frankfurt, Germany.

The aim of this paper is to find a connection between the photoluminescence and the other—mainly structural—properties of undoped GaN epitaxial layers. For this purpose a large number of samples has been investigated at low temperature by photo-excitation. Some characteristic lines have been observed. Their properties will be presented and discussed later on in the text. Two new lines I_1 at 3.476 eV and I_4 at 3.311 eV have been found. A photon energy of 3.476 has been evaluated by Dingle *et al* (1972) as lowest free exciton transition in GaN. Considering the properties of I_1, we suggest that it is more likely the recombination of a bound exciton. From the results of the measurements of reflectance, the lowest free-exciton transition is proposed to be around 3.479 eV.

2. Samples and set-up of the experiment

The GaN epitaxial layers used were grown by the vapour phase epitaxy method on sapphire substrates oriented in the (0001) direction, such as in Maruska and Thietjen (1969). With an improved reaction zone, having a variable cross section, homogeneous large-area epitaxial layers were obtained (unpublished report from Changchun Institute of Physics, China). Purified NH_3 is used as the source of nitrogen while Ga (6N) is transported as its subchloride by reaction with HCl (4N) gas to the reaction zone. The reaction apparatus used is made of fused silica. Laue patterns and the surface morphology of the crystals observed with a scanning electron microscope indicate that the layers are single crystals. The carrier concentrations of the undoped samples as determined by Hall measurements are in the range 1.5×10^{17} to 1.5×10^{18} cm^{-3} at room temperature. The precision of these values may be influenced by grain boundaries and distorted regions of the epitaxial layer close to the substrate. The thicknesses of the layers are about 10 to 60 μm.

The method of the photoluminescence and reflectance measurements are standard. If nothing else is indicated, a 100 W high-pressure mercury lamp is used as an excitation source.

3. Experimental results

According to the shape of the photoluminescence spectra which were measured from about 30 samples, all of the samples can be catalogued into three types. The first type has a broad-band emission see figure 1(A). The second type has a broadened but already structured edge emission, and type three samples exhibit a sharp edge emission as shown in figure 2.

The samples of the first type often have a rough crystal surface. Small hills on the surface can be observed under the microscope, and the Laue patterns of these samples are more or less obscure. The shape of the spectra of these samples is dependent on the exciting photon energy. By exciting by higher-energy photons, a very broad band can be obtained. In some samples the high-energy limit of the luminescence can be more than 3.5 eV (figure 1(A)). In the situation of lower-energy photon excitation (see figures 1(B), (C) and (D)), two sharp lines appear at 3.368 ± 0.002 eV and 3.311 ± 0.002 eV which are called here I_3 and I_4 respectively. The line I_3 was reported by Pakove *et al* (1970), but I_4 is a rather new result. These lines are situated at constant positions, independent of the different samples and the exciting photon energy. They can be directly excited by the incident light, irrespective of whether or not the edge emission

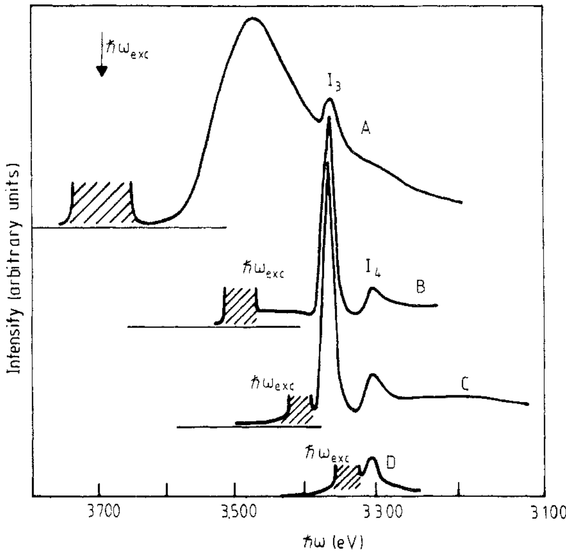

Figure 1. Photoluminescence spectra of the first type of samples for various values of the exciting photon energy ($\hbar\omega_{exc}$). The shape of the spectrum is dependent on $\hbar\omega_{exc}$. By lowering $\hbar\omega_{exc}$ the lines I_3 and I_4 appear clearly. $T = 10$ K.

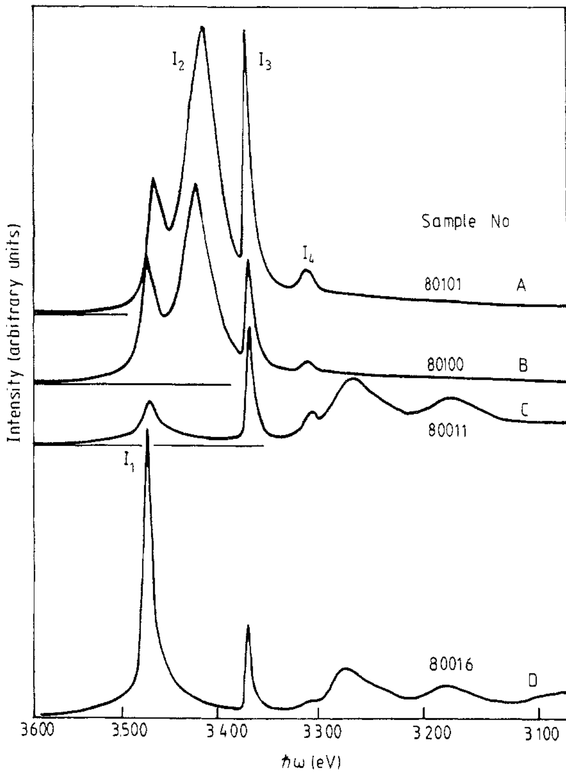

Figure 2. Photoluminescence spectra of the second type of samples A, B and of the third type of samples C, D. $T = 10$ K. $\hbar\omega_{exc} = 3.7$ eV.

appears. If the exciting photon energy is larger than that of I_3, both lines can be excited together. If the exciting photon energy is smaller than that of I_3, but larger than that of I_4, then only I_4 can be excited, as shown in figure 1(D). If the exciting photon energy is smaller than that of I_4, neither of these two lines can be observed. The further properties of them will be discussed in the following paragraphs.

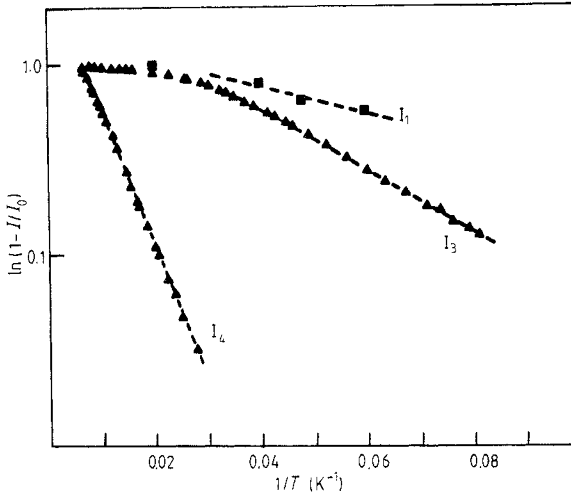

Figure 3. The relationship between the intensities of the lines I_1, I_3 and I_4 and the temperature of the samples. The broken lines correspond to $\ln(1 - I/I_0) \sim 1/T$, where I_0 is the luminescence intensity at 10 K.

Figures 2(A) and (B) show the spectra of the second type of sample which has a broadened edge emission. This type of sample has a relatively smooth surface and a sharp Laue pattern. In the high-energy region of the spectrum there are two clearly resolved but broadened lines, called here I_1 and I_2 respectively. For each sample the energetic position of I_1 and I_2 is independent of the exciting photon energy, but they can shift their positions in different samples. Here it has been found that I_1 shifts in the region of 3.467 eV to 3.476 eV.

In the samples of the second and third type, the lines I_3 and I_4 can still be observed at their constant energies as before, but the intensities of them are much smaller than in the first type of sample. The type-3 samples have the weakest I_3 and I_4 lines, and a very sharp and strong line I_1, as shown in figures 2(C) and (D), but the line I_2 disappears.

In the lower-energy region of the photoluminescence, the broad lines at 3.27 eV, 3.18 eV and 3.09 eV, which have been discussed by Dingle and Ilegems (1971), can be observed in all of our samples. These lines have higher intensities and are better resolved in the type-3 samples. Since they have a mutual energetic distance of 90 meV which coincides with the LO phonon energy in GaN (Dingle and Ilegems 1971), they are assumed to be phonon satellites eventually of I_3. In this paper we limit ourselves to discussing the higher-energy emission lines from GaN only.

The lines I_1, I_2, I_3 and I_4 are all temperature sensitive. Especially, I_1 and I_2 rapidly disappear when the temperature is increased. At about 18 K they are already much weaker than at 10 K. The relationship between temperature and the intensities of I_1, I_3

and I_4 can be described as

$$\ln(1 - I/I_0) \sim 1/T. \quad (1)$$

Here I is the intensity of the lines, I_0 is their intensity at 10 K, and T is the temperature of the samples. Figure 3 shows the experimental results. The curves calculated according to equation (1) are given as broken curves.

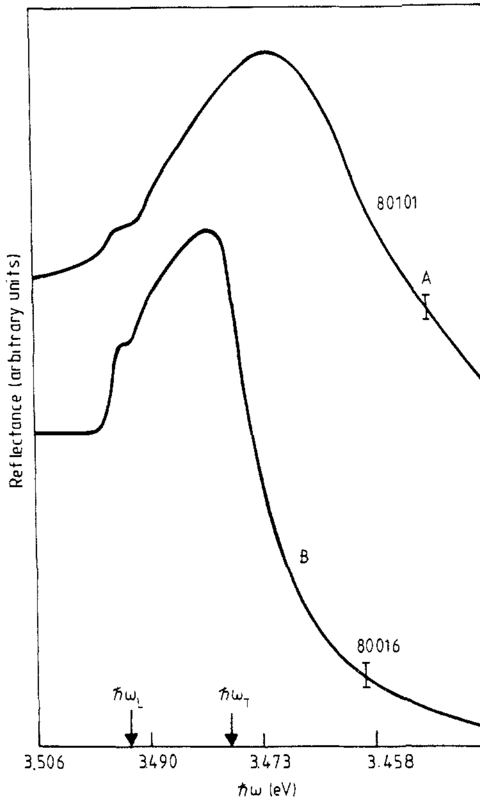

Figure 4. Typical reflectance spectra of the second (A) and third (B) types of the samples. $T = 5$ K.

The reflection spectra of the second and third type of samples were measured at 5 K, for $\boldsymbol{E} \perp \boldsymbol{c}$ and $\boldsymbol{k} \parallel \boldsymbol{c}$. Two typical examples are shown in figure 4.

By comparing the reflection spectrum and the luminescence of the samples, it is found that in type-2 samples the main structure of reflectance is a relative broad peak which shifts together with I_1, and the line I_1 is situated on the top of the peak of the reflection spectrum. In the third type of samples the reflectance shows a narrower peak which has a constant position, and the line I_1 falls on the lower-energy side of the reflectance peak, but not on the top of it.

The relationship between the intensities of lines I_1, I_3 and I_4 and the excitation intensity is given in figure 5. Here a pulsed N_2 laser is used as excitation source. It is found that neither I_1 nor I_3 and I_4 have a linear dependence on excitation intensity (see figure 6). The peaks of them shift their positions with excitation intensity: at higher

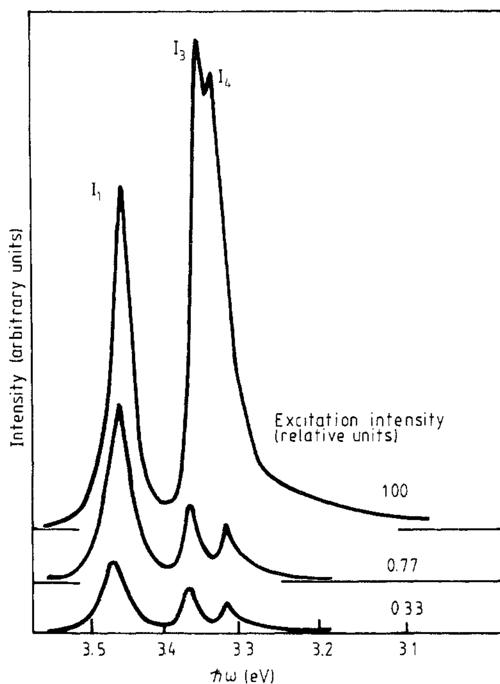

Figure 5. The excitation intensity dependence of lines I_1, I_3 and I_4. Here a N_2 laser is used. $T = 5$ K, $\hbar\omega_{exc} = 3.7$ eV.

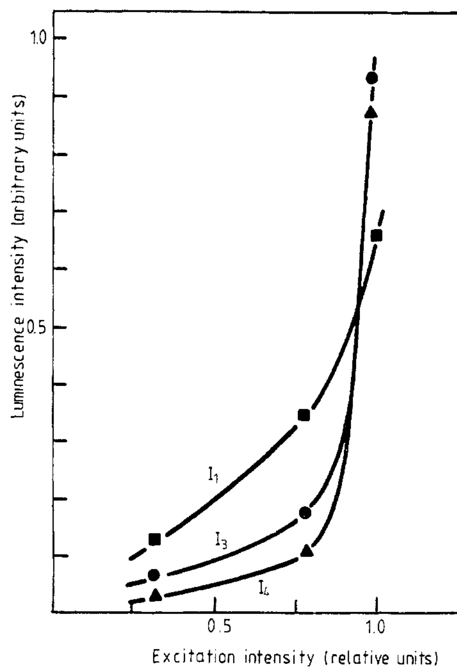

Figure 6. The relationship between the intensities of lines I_1, I_3, I_4 and the intensity of N_2 laser excitation. Same sample as in figure 5, $T = 5$ K, $\hbar\omega_{exc} = 3.7$ eV.

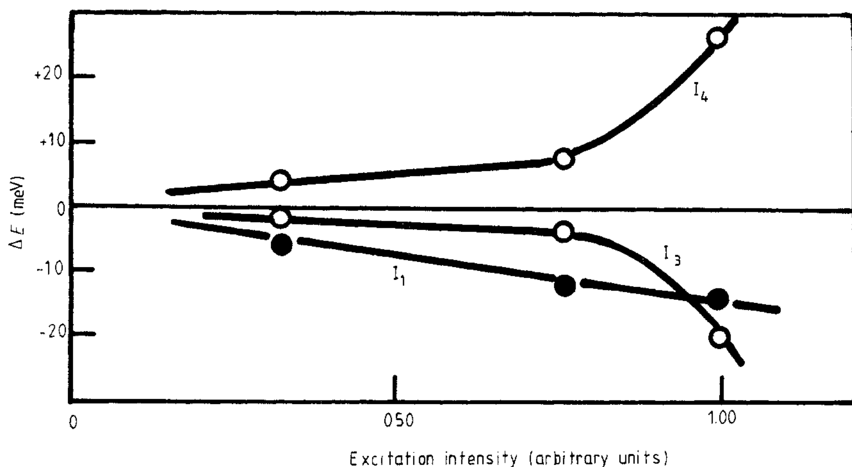

Figure 7. The shift of the energetic positions of lines I_1, I_3 and I_4 with increasing N_2 laser excitation.

excitation I_1 and I_3 shift to the lower-energy side but I_4 shifts to the higher-energy side, as shown in figure 7.

4. Discussion

According to the information from the Laue pattern, the surface morphology, and the emission and reflection spectra of GaN epitaxial layers, it is clear that the samples have different quality of crystal structure. The third type of samples is the most perfect one among them. The results which we have shown in this paper are measured on undoped layers, and so the most probable defects of the crystal, which can be introduced during the expitaxial process, are vacancies of nitrogen and the mismatch and stress between the GaN layer and the sapphire substrate.

The lines I_3 and I_4 appear in all of our samples. They have a constant energetic position which does not change from sample to sample. We suggest that they are connected with some localised energy levels caused by imperfections in the crystal. We propose that I_3 is attributed to the neutral donor of the nitrogen vacancy. Its energy position shift at higher excitation intensity may then eventually be attributed to the formation of larger multiexcitonic complexes (Kosai and Gershenzon 1973). Since the energy position of line I_4 shifts to the higher-energy side of the spectrum with increasing excitation intensity, it is assumed that I_4 is caused by donor–acceptor pair transitions. The thermal dissociation energies of I_3 and I_4 are evaluated as $\Delta E_3 = 3.4$ meV and $\Delta E_4 = 14.4$ meV. These values are not contradictory to our explanation.

The line I_1 has the highest energy in the emission spectra of epitaxial GaN. It ought to be pointed out that the energetic position of I_1 at 3.476 eV is a new result, which is about 10 meV higher than the previous results of Dingle *et al* (1971). An energy of 3.476 eV is already the value of the free exciton transition in GaN, as suggested by Dingle *et al* (1972). According to the following reasons, we suggest that I_1 is not due to the recombination of free excitons, but comes from the annihilation of an exciton bound at a shallow localised energy level (Grimmeiss and Monemar 1970);

(i) The line I_1 can change its energy position from sample to sample.

(ii) The intensity of I_1 is very strongly dependent on the temperature of the sample. This means that I_1 has a rather low activation energy. It is deduced from figure 3 to be $\Delta E_1 = 1.9$ meV.

(iii) The recombination of free excitons is not expected to have such a strong intensity, if one bears in mind that even in a high-quality crystal of ZnO, which is very similar to GaN, the contribution of the free exciton to the luminescence is very small (Tomzig and Helbig 1976). In addition, a high density of imperfections is obvious in GaN epitaxial layers, as pointed out before.

(iv) The nonlinear dependence of the intensity of I_1 and the shift of the energetic position of line I_1 with excitation intensity (see figures 5, 6 and 7 respectively) are not readily explained in terms of a free exciton transition.

If one adopts the above arguments, the question must be presented: which energy belongs to the free exciton in GaN? The reflection spectra of figure 4 give a clear answer. Figure 4(B) is a typical reflection spectrum of the third type of samples. Excitonic reflection spectra have been evaluated for a rather long time, (see e.g. Hopfield 1963, Lagois and Hümmer 1975, Stössel and Wagner 1978, Broser *et al* 1978). If we follow the ideas developed by Hopfield (1963), we may assume that the small peak at 3.494 ±

0.002 eV is caused by an exciton free surface layer and corresponds to the eigenenergy of the longitudinal A exciton. The transverse eigenenergy is expected from figure 4(B) to be situated around 3.479 ± 0.002 eV, resulting in a value for Δ_{LT} of 15 ± 5 meV. The shift of the maximum of the reflection spectrum in figure 4(A) might be due to a stronger damping of the exciton state, caused by a less perfect crystal structure. Some smaller reflection structures situated above 3.500 eV (not shown here) will be discussed in a forthcoming paper.

The line I_2 has a relatively broad and symmetric form, and shifts for different samples, but disappears in the third type of samples. Till now we have no appropriate explanation for it. We now believe that it is caused by imperfections introduced by the stress between the GaN layer and the substrate.

Concerning the broad emission band of type-1 samples, it can be assumed that the lattice is strongly distorted. The free exciton and bound exciton no longer exist as discrete energy levels. The luminescence is proposed to be due to transitions between impurity band states.

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References

Broser I, Rosenzweig M, Broser R, Richard M and Birkicht E 1978 *Phys. Status Solidi* (b)**90** 77
Cunnigham R D, Brander R W, Knee N D and Wickenden D K 1972 *J. Luminesc.* **5** 21
Dingle R and Ilegems M 1971 *Solid State Commun.* **9** 175
Dingle R, Sell D D, Stokowski S E, Dean P J and Zterrstrom R B 1971 *Phys. Rev.* B**3** 497
Dingle R, Sell D D, Stokowski S E and Ilegems M 1972 *Phys. Rev.* B**4** 1211
Grimmeiss H G and Monemar B 1970 *J. Appl. Phys.* **41** 4054
Hopfield J J 1963 *Phys. Rev.* **132** 563
Jacob G and Bois D 1977 *Appl. Phys. Lett.* **30** 412
Kosai K and Gershenzon M 1973 *Phys. Rev.* B**9** 723
Lagois J and Hümmer K 1975 *Phys. Status Solidi* (b)**72** 393
Maruska H P and Thietjen J J 1969 *Appl. Phys. Lett.* **15** 327
Pakove J I, Berkeyheiser J E, Maruska H P and Wittke J 1970 *Solid State Commun.* **8** 1051 (1970 *Proc. 10th Int. Conf. on Physics of Semiconductors, Cambridge, Mass.* p 593)
Stössel W and Wagner H J 1978 *Phys. Status Solidi* (b)**89** 403
Tomzig E and Helbig R 1976 *J. Luminesc.* **14** 403