Optical investigation of deep defects in GaN epitaxial layers grown on 6H-SiC

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Photoluminescence (PL) has been used to study GaN layers, which were grown by the sublimation sandwich technique on 6H-SiC substrates. The promising quality of the samples, which have a lattice mismatch of 3·5%, is demonstrated by the high intensity and the small half width (2 meV) of the donor bound exciton which is comparable to that for metalorganic vapour phase epitaxy grown layers. Fourier transform infrared photoluminescence spectroscopy was used to search for 3d elements (deep defects) which are incorporated as natural contaminants during the epitaxial growth. An emission with a no phonon line at 1·3 eV was observed, which is proposed in the literature to be caused by an internal 3d transition of Fe^{3+}, and also two additional strong emissions with sharp no phonon lines at 1·19 and 1·04 eV. The PL measurements show that the emission at 1·19 eV is due to an internal 3d transition of a d^2 system. The no phonon line at 1·04 eV belongs to an internal 3d transition of a d^1, d^2, or d^7 system, possibly Ti^{2+}, Ti^{3+}, V^{3+}, or Co^{2+}. MST/3315

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Introduction

The materials ZnSe, SiC, and GaN are three intensively studied candidates for short wavelength optical applications.[1] Considerable progress has been made in recent years regarding the quality of the samples because of improved growth techniques. Blue light emitting diodes (LEDs) manufactured from SiC are already commercially available. However, all polytypes of SiC have an indirect band gap, so the quantum efficiency of GaN LEDs (GaN has a direct band gap) is a significant improvement over that of SiC LEDs. The prominent material in laser development is ZnSe, but there are considerable problems associated with the device lifetime. Thus GaN might become the optimum candidate, not only for blue LEDs, but also for blue laser devices.

One of the main problems in GaN technology is the selection of the substrate because there is no lattice matched substrate available for epitaxial growth. As the growth of GaN substrate material is rather problematic (high N potential pressure), heteroepitaxy is necessary for GaN crystal growth. In recent years various growth techniques, e.g. molecular beam epitaxy (MBE) or metalorganic vapour phase epitaxy (MOVPE), have been attempted. Usually α-Al_2O_3 substrates in the [0001] orientation are used (lattice mismatch 16%), but epitaxial growth on Si substrates has also been used.[2,3] More closely lattice matched materials for the growth of GaN layers are ZnO and 6H-SiC (3·4% lattice mismatch) substrates.

In the present paper photoluminescence (PL) was used in the spectral region between 0·3 and 3·5 eV to study GaN layers which were grown on 6H-SiC by the sublimation sandwich technique. The promising quality of the samples can be demonstrated by near band gap PL. The main aim of this work is the search for contaminants, incorporated during the epitaxial growth, in the mid infrared (IR) and near IR spectral region. Until recently, little was known about deep defects in GaN. In particular, 3d elements are possible candidates for natural contaminants. They act as deep defects and can thus significantly limit the performance of devices. In addition they can be useful in producing semi-insulating substrate material. Hence the identification of 3d elements and their behaviour in the host is highly important for optimisation of devices. Characteristic, sharp no phonon lines, due to internal electronic transitions within the d shell, are observed in 3d elements. In contrast to most other III–V semiconductors GaN has a wurtzite structure. It is expected that 3d elements are incorporated on Ga sites in GaN and are consequently surrounded by four N nearest neighbours.

Experimental

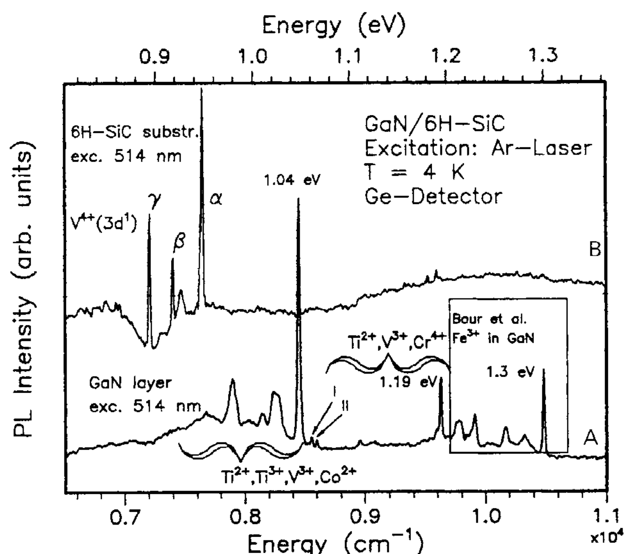
For the growth of GaN, substrates of the 6H polytype of SiC were used, which were grown by the Lely method, and are oriented in the [0001] plane. The GaN layers were grown by a modification of the sandwich technique.[4–6] Details of the growth are reported in Refs. 7 and 8.

For the PL measurements in the near band gap region, a conventional monochromator technique was used. The samples were excited with a Hg–Cd laser. To increase the sensitivity of the PL measurements in the near and mid IR region, Fourier transform infrared (FTIR) PL spectroscopy was carried out using a Bomem DA8.02 Fourier spectrometer, which was equipped with either a Ge detector or an InSb detector. For excitation, either an Ar ion laser with an additional ultraviolet (UV) option or the 647 nm line of a Kr ion laser was chosen. The temperature in the cryostat could be varied between 2 and 300 K. The preliminary Zeeman measurements were carried out using an optical superconducting magnet (up to 15 T) and conventional monochromator technique.

Sample characterisation

X-ray diffraction measurements on the samples show a lattice mismatch of 3·5%. As shown in reflection measurements a free carrier concentration of $2–4 \times 10^{17}$ was determined.[7,8]

The PL measurements were carried out between the band gap region (3·5 eV) and 0·3 eV. The near band gap spectra of the best GaN/6H-SiC samples show a strong emission of the donor bound exciton (D^0X) at 3·47 eV (Ref. 8). Towards lower energy, shallow donor to shallow



A GaN layer, three no phonon lines peaking at 1·3, 1·19, and 1·04 eV can be detected by Ar ion laser (514 nm) excitation; B back side of sample (6H-SiC substrate), well known V^{4+} emissions α, β, and γ can be seen

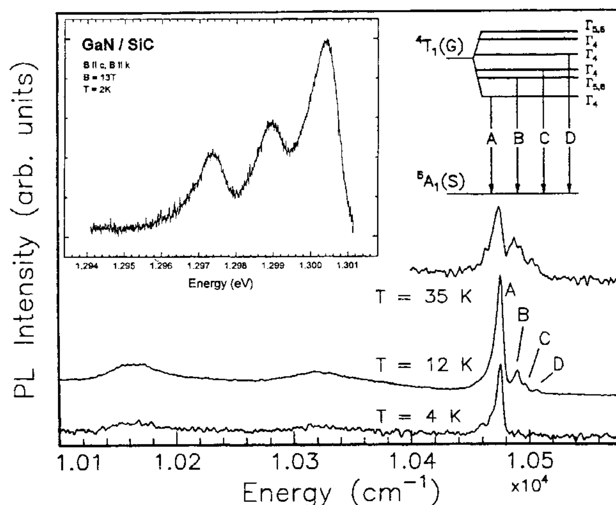
1 Photoluminescence (PL) spectra of GaN/6H-SiC in region 6500–11 000 cm^{-1}

acceptor (D^0A^0) pair transitions are resolved. The ratio of the (D^0X) luminescence to the (D^0A^0) luminescence is a measure of the quality of the samples. Thus the intense appearance of the (D^0X) emission demonstrates the good quality obtainable by the sandwich technique for the present samples. In addition, the exciton half width is less than 2 meV, a value which is comparable or even superior to the half width observed for MOVPE grown samples. In two of the samples a broad emission at 2·2 eV was observed.[7,8] As C doping enhances this emission it was speculated that the recombination is between a shallow donor level and a deep acceptor complex involving C.[9]

Deep defects related to 3d elements in GaN – results and discussion

Figure 1 shows a typical spectrum of GaN samples in the near IR region (spectrum A). For this measurement, the 514 nm (2·41 eV) green line of the Ar ion laser was used, i.e. below band gap excitation. In this spectrum three characteristic no phonon lines can be distinguished at 10 475 cm^{-1} (1·3 eV), 9624·5 cm^{-1} (1·19 eV), and 8445 cm^{-1} (1·04 eV) with their corresponding phonon side bands. Depending on the sample these values can shift slightly. In addition, two weak phonon lines appear at 8556 and 8600 cm^{-1}. As shown below, these weak emissions (labelled I and II) belong to additional 3d related defect emissions. Down to 0·3 eV, no other sharp lines can be observed in the samples. To ensure that these defect related emissions are due to the GaN layer PL measurements were also performed on the 6H-SiC substrate (*see* Fig. 1, spectrum B). Only typical V^{4+} related lines α, β, and γ[10] could be clearly observed and no trace of the GaN related emission lines shown in spectrum A could be seen.

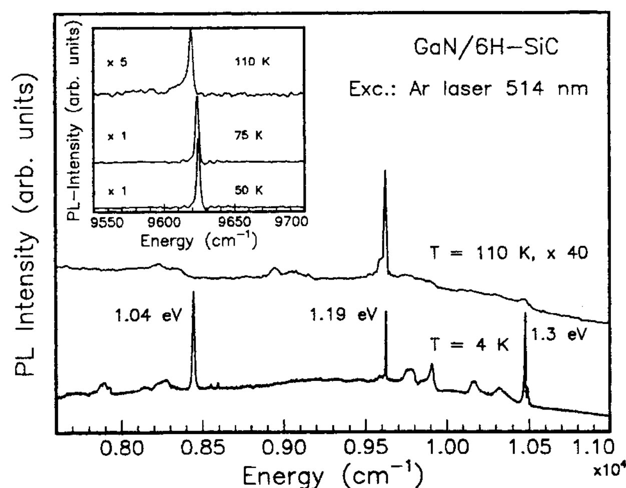
The spectrum in the box with the strong no phonon line peaking at 10 475 cm^{-1} (1·299 eV) was reported by Maier *et al.*[11] and Baur *et al.*[12] in their GaN samples which were grown on a sapphire substrate. From electron paramagnetic resonance (EPR), optically detected magnetics resonance (ODMR), and temperature dependent PL studies, they attributed this emission to the $^4T_1 \rightarrow {}^6A_1$ internal 3d transition of Fe^{3+}. The present data confirm that the transition is due to a d^5 system.



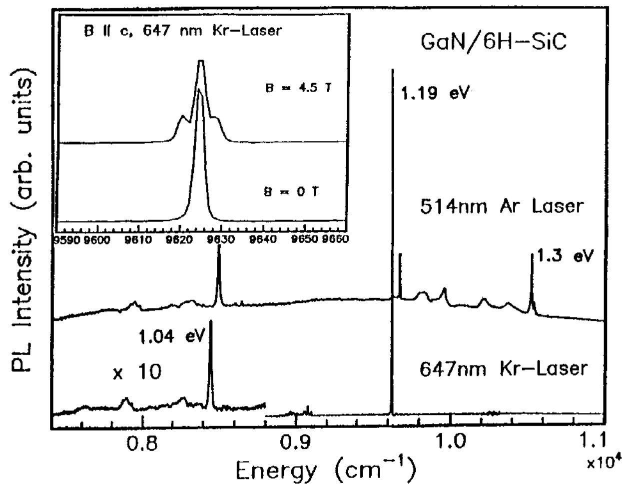
2 Detailed PL spectrum of 1·3 eV emission, interpreted in literature as $^4T_1 \rightarrow {}^6A_1$ spin flip transition of Fe^{3+} – inset shows spectrum taken at high magnetic field (13 T)

Figure 2 shows a detailed PL spectrum of the 1·3 eV (10 475 cm^{-1}) emission together with part of the phonon side band. In the two spectra taken at higher temperatures the appearance of the three hot lines at 10 490 (B), 10 497 (C), and 10 506 cm^{-1} (D) can be clearly observed. These were previously reported in Ref. 12. In the level diagram the observed transitions are indicated by arrows.

The lineshape of the no phonon line with a maximum at 10 475 cm^{-1} (1·299 eV) is asymmetric with a tail on the low energy side. As the half width is about 7 cm^{-1}, Zeeman measurements are rather problematic. Preliminary Zeeman measurements for B ∥ c up to a magnetic field of 13 T show anisotropic splitting in at least three components (*see* inset, Fig. 3). Corresponding to Fe^{3+} in ZnO, a sixfold splitting should be resolved. However, according to Ref. 13, three of the lines are expected to be very weak and therefore cannot be readily distinguished under the relatively broad lines. Similar intensities and the dominance of three transitions are found in Fig. 3 of Ref. 13. Thus the Zeeman results are compatible with an attribution to Fe^{3+}.

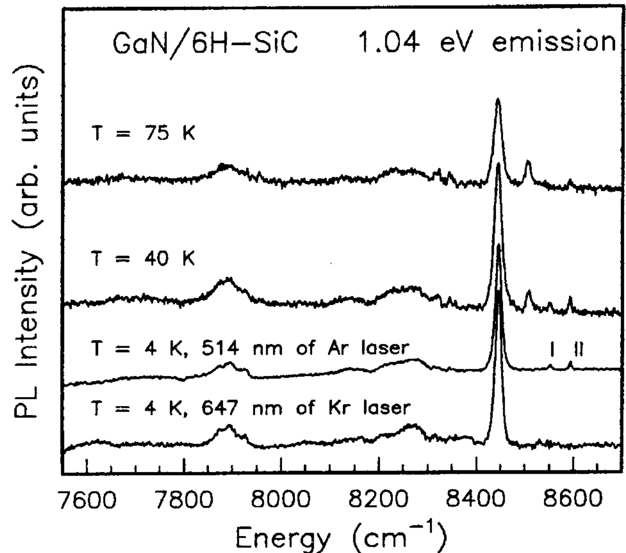


3 Two PL spectra of GaN/6H-SiC taken at 4 and 110 K, with inset showing three detailed spectra of no phonon line at 1·04 eV detected at high temperatures – half width remains <4 cm^{-1} even at temperatures >110 K



for clarity spectra are shifted, when sample is excited by Ar laser, by 50 cm^{-1}, hence scale on x axis corresponds to sample excited by Kr laser

4 Two PL spectra of GaN/6H-SiC excited by either Ar ion laser (514 nm, 2·41 eV) or Kr ion laser (647 nm, 1·92 eV), i.e. both below band gap excitation; for Kr laser excitation 1·04 eV emission increases by more than factor of 5 – inset shows two spectra, at zero magnetic field and at 4·5 T, illustrating threefold splitting of ground state ($S = 1$)



5 Four spectra of 1·04 eV emission observed in GaN: spectrum taken at 4 K with Kr ion laser (647 nm) does not show two lines labelled I and II, which are apparent in spectrum detected by Ar ion laser (514 nm) at 4 K – as temperature increases, as seen in spectra at 40 and 75 K, one hot line appears

From low temperature (4 K) time resolved PL a decay time of 8 ms was determined. Such a long decay in the millisecond range is typical for a spin forbidden $^4T_1 \rightarrow {}^6A_1$ transition of a d^5 system, e.g. Fe^{3+}. This is in excellent agreement with the results on Fe^{3+} in InP,[14] GaAs,[15] and ZnS (Ref. 16) and on Mn^{2+} in GaP,[17] for which decay times in the millisecond range were observed.

The second defect related emission consists of a strong no phonon line at 9625 cm^{-1} (1·19 eV) (*see* Fig. 1, spectrum A) and has a rather weak phonon coupling compared with the other two defect emissions. The no phonon line at 1·19 eV was first reported by Baur *et al.*[12] in their GaN samples grown on sapphire. They tentatively assigned this emission to Cr^{4+}. The present results indicate that this may not be the correct assignment.

This defect shows a few features of interest as follows. Figure 3 shows two spectra of the three emissions. These spectra were taken using the 514 nm line of the Ar ion laser at 4 and 110 K. Only the emission at 1·19 eV can be clearly observed in the high temperature spectrum. From the other two emissions only a weak trace of the 1·3 eV emission can be resolved at about 110 K. This observation indicates that the three emissions do not belong together.

The half width of the no phonon line at 1·19 eV is 1·2 cm^{-1} in the present samples at 4 K. In temperature dependent measurements the emission could be observed at temperatures higher than 110 K (*see* inset of Fig. 3). The line width at 110 K remained less than 4 cm^{-1}.

In Fig. 4 two spectra are compared which were excited using either the 647 nm line of the Kr ion laser or the 514 nm line of the Ar ion laser. A very strong enhancement of the 1·19 eV emission was observed (by at least a factor of 5) in the spectra that were excited with the Kr ion laser. This indicates an excitation into an excited state via which the 1·19 eV luminescence intensity is strongly enhanced.

The emission at 9625 cm^{-1} (1·19 eV) shows not only a very weak phonon coupling, but also a line width of the no phonon line which remains sharp up to high temperatures. Three spectra taken at different temperatures are shown in the inset of Fig. 3. In addition no hot line could be resolved with increasing temperature. The line width is only 1·2 cm^{-1} and hence Zeeman measurements are possible. These are shown in the inset of Fig. 4 in which the preliminary Zeeman measurements show threefold splitting for B II c. No thermalisation can be seen in the ground state.[18]

In Zeeman measurements, a spin triplet ($S = 1$) ground state is observed. At 2 K only one no phonon line is detected. The only configuration that agrees with these results is a d^2 system. The possible transition metal contaminants are Cr^{4+}, V^{3+}, and Ti^{2+}; Sc^{+} can be excluded as a natural contaminant, because it has a very low solubility in III–V semiconductors. In addition, the authors are not aware of any literature reports of luminescence of Sc^{+} (d^2).

From the reflection measurements it is assumed that the samples are n type. Thus, an emission due to Cr^{4+} is only possible when a Cr^{3+}–Cr^{4+} charge transfer takes place. This is improbable. As the excitation with the 647 nm red light of the Kr ion laser below the band gap (strong enhancement of PL intensity) indicates an excited state in the band gap at about 1·9 eV, the emission is due to a 3d element that is already in this charge state. Therefore an attribution to an internal 3d transition of Cr^{4+} can probably be excluded. Thus the only transition metal contaminations that can be responsible for the emission are Ti^{2+} and V^{3+}.

Although the emission of 1·19 eV shows a weak phonon coupling and a strong temperature stability, which is typical behaviour for rare earth ions, attribution to a rare earth element is excluded. There are three rare earth elements: Pr^{3+}, Nd^{3+}, and Yb^{3+} with internal 4f laser transitions close to 1·19 eV (*see* Ref. 19). However, for these elements, more than one transition would be expected at low temperature, because the crystal field states should split by spin orbit coupling. In addition it is highly unlikely that a rare earth contaminant will be found in an undoped semiconductor.

Figure 5 shows four spectra of the no phonon line peaking at 8845 cm^{-1} (1·04 eV) and the corresponding phonon side band, which were either detected at different temperatures or excited by different lasers. In the upper three spectra the samples were excited with the 514 nm line of the Ar ion laser. For comparison, the lowest spectrum was observed by excitation with the 647 nm line of the Kr

ion laser. In the 4 K spectrum excited with the Ar laser the two lines labelled I (8565 cm^{-1}) and II (8600 cm^{-1}) were observed. They do not appear in the spectra excited with the Kr laser, so they must belong to another defect. From the temperature dependent measurements it is difficult to conclude whether the two lines belong together or not. It is assumed that the emissions must belong to small traces of other internal 3d transitions of a 3d element.

The line width of the 1·04 eV emission is 15 cm^{-1}, which is very broad for Zeeman measurements. No shift of the maximum for B ∥ c was observed up to 7 T. The maximum remained in the same position; only the half width increased by a factor of 1·5. It is probable that an unresolved splitting leads to this line broadening. With an increase in temperature a hot line 64 cm^{-1} higher in energy appears. As only one transition is observed at 4 K the emission must belong to an internal 3d transition of a d^1 (ground state ^2E), d^2 (ground state $^3A_2$), or d^7 (ground state $^4A_2$) system, which show no splitting of the ground state in T_d symmetry. The possible transition metal contaminations are Ti^{3+}, Ti^{2+}, V^{3+}, and Co^{2+}.

Transitions involving Sc^+ and Sc^{2+} can be excluded for the reasons mentioned above. An emission due to Ni^{3+} can also be excluded. According to the rule of Langer and Heinrich[20] (for a compilation of data *see* also Ref. 21) the occupied state in the dark should be Ni^+, so a charge transfer to Ni^{3+} is improbable.

Conclusions

Photoluminescence (PL) spectroscopy was carried out on GaN samples which were grown on 6H-SiC substrates by the sublimation sandwich technique. Very intense excitonic (D^0X^0) emissions could be observed in the samples, which have line widths of less than 2 meV. This indicates the promising quality of the samples. Three no phonon emissions were observed in the near infrared region, due to internal transitions in the d shell of 3d elements. The present results confirm the attribution of the no phonon line at 1·3 eV to a d^5 configuration, possibly Fe^{3+}. The results also show that the second emission, peaking at 1·19 eV, is either Ti^{2+} related or V^{3+} related. The emission has a sharp line width even at temperatures higher than 110 K and the PL intensity can be strongly enhanced using below band gap excitation with the 647 nm line of a Kr ion laser. Only one no phonon line is observed at low temperature so the third no phonon line at 1·04 eV must belong to a d^1, d^2, or d^7 system. Possible transition metal contaminations are Ti^{2+}, Ti^{3+}, V^{3+}, and Co^{2+}.

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