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Optical properties of electron-irradiated GaN

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The electronic structure of defects produced by 2.5-MeV electron irradiation and their effect on optical properties of GaN are investigated using photoluminescence (PL) and optically detected magnetic resonance (ODMR) techniques. The electron irradiation is shown to produce, in particular, a deep PL band with a no-phonon line at around 0.88 eV followed by a phonon-assisted sideband. We suggest that this emission is caused by an internal transition between excited and ground state of a deep defect. The excited state is a multiple-level state, as revealed from temperature dependent PL and level anti-crossing experiments. The electronic structure of the 0.88 eV defect is shown to be sensitive to the internal strain in the GaN epilayers. The ODMR studies reveal that the principal axis of the defect coincides with the c-axis of the host lattice and should therefore be either an on-site point defect or an axial complex defect along the c-axis.

1 Introduction

Recent years have witnessed an explosion of the amount of research work devoted to III-nitrides, motivated by the desire for efficient light emitters operating in the blue and ultraviolet spectral regions. An achieved breakthrough [1] in GaN technology, providing GaN material with p-type conductivity, was immediately followed by a realization of light emitters [2] [3]. A full exploitation of the abilities provided by the III-nitrides for blue light emitting devices requires an identification and control of impurities and native defects in the material. However, in spite of the recognition of the importance of GaN, many of its defect related properties and doping issues are still not yet well understood. In particular, the nature of defects responsible for the residual n-type conductivity of GaN, suggested to be e.g. native defects (nitrogen vacancies) [4] or residual impurities [5] [6] still remains a topic of many debates. It is known that the concentration of native defects can be varied by using electron irradiation [7] [8], making this method very powerful for investigations of defect-related issues.

In this work we investigate the electronic structure of defects produced by 2.5-MeV electron irradiation and their effect on optical properties of wurtzite GaN, by using photoluminescence (PL) spectroscopy and optically detected magnetic resonance (ODMR) measurements. The electron irradiation is shown to activate, in particular, a deep PL band with a no-phonon line at around 0.88 eV followed by a phonon-assisted sideband. We suggest that this emission is caused by an internal transition between an excited and the ground state of a deep defect. The excited state is a multiple level state, as revealed from temperature dependent PL and level anti-crossing experiments. The electronic structure of the 0.88 eV defect is shown to be sensitive to the internal strain in the GaN epilayers. From the ODMR studies, the principal axis of the defect is shown to coincide with the c-axis of the host lattice and should therefore be either an on-site point defect or an axial complex defect along the c-axis.

2 Experimental

The wurtzite GaN epilayers used in this study were grown by metal organic vapor phase epitaxy (MOVPE) on c-plane 6H SiC or sapphire substrates at a temperature of about 1000 °C. The thickness of the GaN epilayers is about 2 μm. Intentionally undoped layers with n-type conductivity, compensated GaN layers and Zn- or Mg-doped GaN epilayers with p-type conductivity were chosen for this study to analyze a possible effect of the Fermi level position on the defect formation during electron irradiation. Electron irradiation was performed at room temperature by 2.5 MeV electrons from a Van de Graaff accelerator to a dose of up to 4×10^{18} cm^{-2}.

Since the expected penetration range for 2.5 MeV electrons in GaN is about a few millimeters, electron-induced damage can be regarded to be uniformly produced through the 2 µm-thick GaN films. During irradiation samples were mounted on a water-cooled holder to avoid any possible heating.

The PL and reflectance measurements were done using an Oxford Instruments SM4000 cryomagnetic system allowing measurements in the range from 1.8 K up to 300 K. PL was excited by the 351 nm line of an Ar^+ ion laser with an excitation density of 0.2 W/cm^2. The used excitation density was sufficiently low to avoid any heating of the sample during the measurements, judging from the performed measurements using much higher excitation densities of up to 4 W/cm^2. The penetration depth of the exciting light was about 0.1 µm. For reflectance measurements a quartz halogen lamp was used as an excitation source. PL emissions were dispersed using a 0.8 m SPEX double grating monochromator and detected using a conventional lock-in technique by a nitrogen-cooled North Coast Ge detector in the near infrared region, or a GaAs photomultiplier tube in the visible region. The ODMR experiments were done at the X-band (9.23 GHz) using a modified Bruker ESR spectrometer, equipped with a TE_{011} microwave cavity. The ODMR signal was obtained by detecting a synchronous change in the PL with on-off modulation of the microwave field. The level anticrossing (LAC) experiments were done with the aid of the ODMR system. A modulation of magnetic field was employed, giving rise to a derivative line shape of the LAC signal.

3 Experimental results

Figure 1 and Figure 2 demonstrate the irradiation-induced transformation of the PL spectra recorded from GaN epilayers with different conductivity. One of the main effects observed due to electron irradiation is an appearance of several PL bands in the near infrared (NIR) spectral region, including (i) broad emissions spreading over a wide spectral range from 0.70 to 1.1 eV and peaking at ≈ 0.93 eV, and (ii) a characteristic PL band having a sharp no-phonon (NP) line at ≈ 0.88 eV followed by a richly structured phonon subband. Both emissions have previously been reported in compensated GaN epilayers subjected to 2.5 MeV electron irradiation [8]. The 0.93 eV PL has been tentatively ascribed to a complex defect containing an interstitial Ga. No explanation on the origin of the 0.88 eV emission has been given so far. Below we will discuss properties of the 0.88 eV PL emission only. (A detailed analysis of the photoluminescence transformation induced by electron irradiation will be presented elsewhere [9]).

As is clear from the Figure 1 and Figure 2, the 0. 88 eV PL band strongly overlaps with the 0.93 eV emission. However, by changing excitation conditions it is possible to separate contributions from each emission and thus quantitatively determine the dependence of their intensities on the irradiation dose. In particular, we have found that only the 0.93 eV emission can be efficiently excited when using below band gap excitation. This is demonstrated in Figure 3, where we compare the PL spectra recorded from the same compensated sample under above band gap (3.54 eV) and below band gap (1.57 eV) excitation conditions, respectively. The PL spectrum measured under the below band gap excitation shows the true shape of the 0.93 eV emission and can be used to extract the spectral shape of the 0.88 eV PL.

The 0.88 eV PL is observed in all investigated irradiated structures independent on the conductivity and the doping of the starting GaN crystals. However, in the case of compensated or p-type GaN the 0. 88 eV emission is activated by the irradiation with a dose as low as 1×10^{17} cm^{-2} - see Figure 2, whereas a rather high dose (3×10^{18} cm^{-2}) of electron irradiation is required to activate the 0.88 eV emission in n - type GaN - see Figure 1. After being activated, the intensity of the 0.88 eV emission is found to be practically independent on the irradiation dose for all types of GaN material.

The position of the NP line is sample dependent and changes from 0.868 eV for GaN/SiC epilayers up to 0.882 eV for some of the GaN/ Al_2O_3 samples - see Figure 4. From the reflectance measurements performed on the same samples, the observed variation of the NP line position is found to correlate with the change of the GaN band gap. The variation of the band gap of the GaN epilayer is known [10] [11] to be caused by the internal strain in GaN epilayers developed due to the lattice mismatch and difference in thermal expansion coefficients between the GaN epilayer and foreign substrate (SiC or sapphire).

An increase in measuring temperature causes an appearance of new hot PL emissions with the position of the NP line (NP*) shifted towards higher energies by ≈ 2 - 4 meV with respect to the 0.88 eV emissions - see Figure 4. The value of the shift correlates with GaN bandgap variation. This hot PL emission becomes more pronounced at elevated temperatures and even dominates the photoluminescence for the GaN/SiC epilayers - as shown in Figure 4. The hot PL exhibits exactly the same phonon structure as the 0.88 eV band, implying that both PL transitions originate from the same center. Moreover, the performed analysis of the Arrhenius plot of the ratio between the integrated intensities of NP* and NP provides the same activation energy of the hot PL, $E_a \approx 2 - 4$ meV, as determined from the difference in the spectral positions of the NP and NP* lines. This further confirms the assignment of the both PL transitions to the same radiative center.

A further raise in temperature leads to a quenching of the overall PL intensity with a rather low (< 30 meV) activation energy. Unfortunately, the accuracy of this estimated value is rather poor due to a strong overlapping with the background 0.93 eV PL.

4 Discussion

Based on the results obtained we propose that the 0.88 eV emission originates from an internal electron transition between an excited and the ground state of a deep defect. The energy position of the defect-related ground and excited states can be estimated taking into account that the PL thermal quenching occurs with the activation energy ≤ 30 meV. This locates the lowest excited state of the defect within 30 meV from the conduction band and, consequently, locates the ground state of the defect at approximately E_c — 910 meV. The appearance of the defect-related hot PL at elevated temperatures, as shown in Figure 4, indicates the existence of higher lying excited states of the defect.

The proposed model is additionally supported by the observed correlation between the position of the NP line of the 0. 88 eV emission and a strain-induced variation of the GaN bandgap - Figure 4. The ground state of the deep center is usually rather localized and thus is insensitive to the strain field. The observed shift of the spectral position of the NP-line, as well as a change in the splitting between the excited states, indicate that excited states involved in the recombination are rather shallow and located close to the conduction band, since they follow the strain-induced change of the band gap between different GaN layers [4].

The additional information about the electronic structure of the defect involved in the PL process can be obtained from magnetooptical measurements. Figure 5 demonstrates the dependence of the PL intensity detected at 0.875 eV on an applied magnetic field. As it is clear from the figure, resonance-like changes in the PL intensity are detected at magnetic fields around 150 G and 300 G. Such resonance-like changes in emission intensity induced by a magnetic field, known also as level anticrossings (LAC), are observed when two coupled levels are brought into coincidence by an external magnetic field and are caused [12] by a repelling between the approaching magnetic subblevels. The observation of the LAC features for the 0.88 eV band indicates that the corresponding defect excited states should contain more than two magnetic subblevels.

The origin of defects responsible for the 0. 88 eV emissions is a subject of ongoing studies employing the ODMR technique. According to angular dependence studies of ODMR spectra, measured by monitoring the change of the 0.88 eV PL, the defect maintains the principal symmetry-axis along the c-axis of the host lattice and should therefore be either an on-site point defect or an axial complex defect along the c-axis. Since the PL can be detected in all investigated structures independent on doping, some common residual radiation-activated impurities or native defects/complexes created by electron irradiation may be involved in the recombination process. From theoretical calculations of energy levels associated with native defects in GaN [5] [13], isolated vacancies or antisite defects are unlikely responsible for the 0.88 eV emission.

It should be pointed out that the 0.88 eV PL is observed with comparable intensity in all structures subjected to the highest dose electron irradiation, independent on the conductivity of the as-grown crystals. Thus the observed difference in PL activation between the n-type (see Figure 1) and compensated or p-type (see Figure 2) GaN probably reflects the sensitivity of the 0.88 eV emission to the Fermi level position in the sample, which can be modified by electron irradiation.

5 Conclusions

In conclusion, we have investigated the electronic structure of defects produced by the 2.5-MeV electron irradiation in GaN epilayers, by using photoluminescence and optically detected magnetic resonance techniques. We have shown that the electron irradiation causes an appearance of several PL bands in the near infrared region, including a characteristic PL emission with a no-phonon line at around 0.88 eV followed by a phonon-assisted sideband. We suggest that this emission is caused by an internal transition between an excited and the ground state at a deep defect. The excited state is shown to be a multiple level from temperature dependent PL and level anti-crossing experiments. The electronic structure of the 0.88 eV defect is shown to be sensitive to the internal strain in the GaN epilayers. From the ODMR studies of the defect symmetry, the defect should be either an on-site point defect or an axial complex defect along the c-axis.

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FIGURES

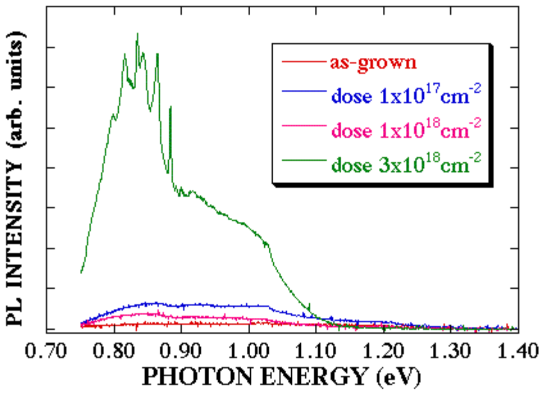

Figure 1. Effect of the electron irradiation on the NIR PL spectra from GaN epilayers with n-type conductivity.

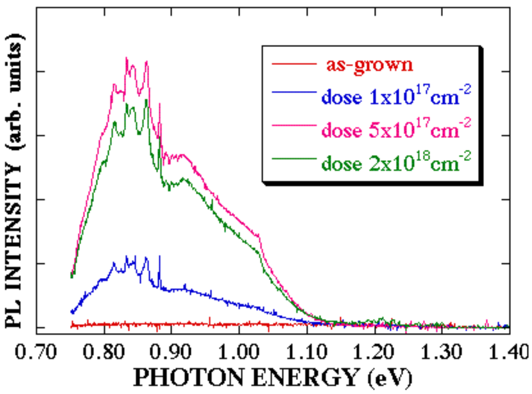

Figure 2. Effect of the electron irradiation on the NIR PL spectra from GaN epilayers with p-type conductivity.

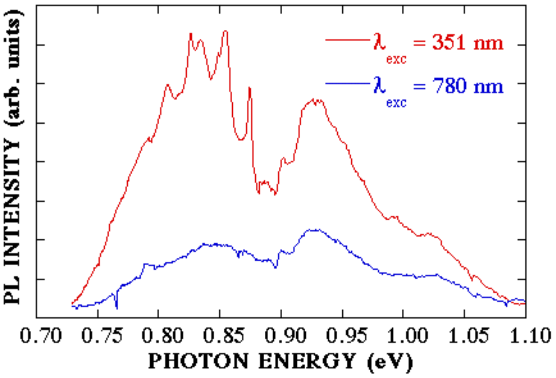

Figure 3. PL spectra of the compensated GaN epilayers irradiated with a dose 1x 10 ^{18} cm^{-2}. Spectra were measured using above band gap excitation of the 351 nm line from an Ar^{+} laser (red curve) and below band gap excitation of 780 nm (blue curve) from a tunable Ti-sapphire laser, respectively.

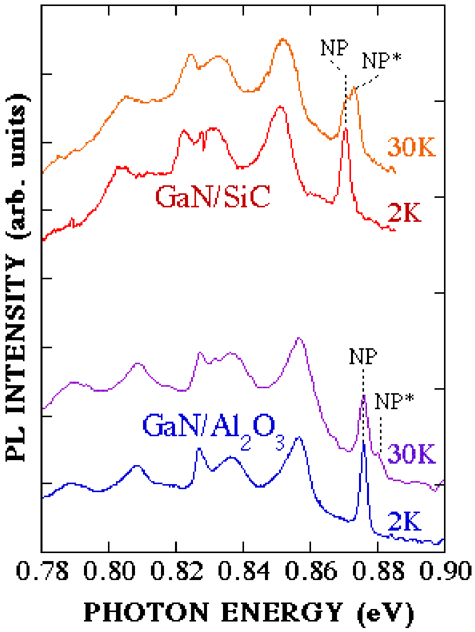

Figure 4. Temperature dependent PL spectra of GaN epilayers grown on SiC and sapphire substrates, respectively. The NP* denotes the no-phonon line of the hot emission, observed at elevated temperatures,

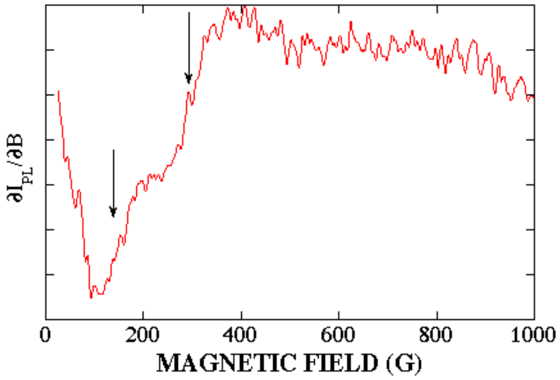

Figure 5. The dependence of the PL intensity (I_{PL}) on an applied magnetic field (B) detected at 0.875 eV for GaN/Al_2O_3 epilayer. The magnetic field was parallel to the c-axis of the GaN epilayers. The derivative spectrum, shown in this Figure, was measured using a differential technique by modulating the applied magnetic field with a frequency of a few kHz.