Effect of internal absorption on cathodoluminescence from GaN

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We have studied optical properties of GaN grown on sapphire by metalorganic chemical vapor deposition in the near band-edge energy range by cathodoluminescence. A large shift of the band-edge luminescence to lower energies is induced by increasing the beam energy. The free exciton position shifts about 20 meV when the beam energy is increased from 5 keV to 25 keV at room-temperature. The effect is explained by internal absorption caused by an exponential absorption tail at the band-edge. An Urbach parameter of about 30 to 40 meV for the exponential band-tail in our samples is estimated by comparing experimental with simulated spectra.

1 Introduction

Luminescence methods, photoluminescence (PL) and cathodoluminescence (CL), are widely used to study the optical properties of GaN and other wide band-gap III-V nitrides. In particular strain [1] [2], composition [3] [4] and electric fields [5] [6] have been studied by the analysis of the excitonic transitions. The advantage of CL is the spatial resolution of this SEM based method and its applicability to materials with band-gap energies greater than those accessible by laser excitation. When studying GaN by CL in the near-band-edge photon energy range we observed a strong peak shift to lower photon energies when the beam energy is increased (Figure 1). This effect had been observed before [7]. The authors speculated that it was caused by strain relaxation and/or piezoelectric fields. In contrast, it is the purpose of this letter to show that the effect can be explained by internal absorption of the luminescent light.

A peak shift may be observed which increases with higher beam energies, and hence greater penetration depth, because an exponential absorption tail at the band-edge cuts the transmission at lower photon energies. We have compared the measured spectra with simulations in order to estimate the Urbach parameter for the exponential tail.

2 Sample Growth

The samples used in this study were undoped 2 μm thick GaN layer grown by metalorganic chemical vapor deposition (MOCVD) on c-plane sapphire. The layers show good structural properties as observed by x-ray diffraction. The full width at half-maximum (FWHM) of the (0002) rocking curve was about 0.1°.

3 Experimental

A home-built system, fitted to a Jeol JSM-35CF scanning electron microscope equipped with an Oxford LN$_2$ cryo-stage, was used for CL measurements. The luminescence was collected by an elliptical mirror with focusing optics and analyzed by a Spex 0.22 m double monochromator equipped with 1200 gr/mm gratings (resolution 0.2 nm). All windows and lenses were UV transparent. Light intensity was measured using the DC current signal of a GaAs photomultiplier tube and was not corrected for the spectral sensitivity of the system. A defocused electron beam, with diameter of about 100 μm, was used when recording a CL spectrum. The beam current was limited to a level at which the luminescence intensity was still proportional to it.

4 Results

4.1 Beam energy dependence of exciton spectra

Figure 1 shows the dependence of the room-temperature CL spectra on the beam energy. In the excitonic range the spectra exhibit two superimposed peaks which could be fitted assuming gaussian broadening. At 5 keV the dominating line is a free exciton at 3.419 eV with a line-width (FWHM) of 60 meV. The second 50 meV broad

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line at 3.347 eV is of unknown origin. It is beyond the scope of this paper to further clear up the origin of this line. The free exciton peak shifts to a lower photon energy of 3.401 eV when the beam energy is increased from 5 keV to 25 keV. Simultaniously, the intensity ratio between the two peaks changes. At 5 keV the intensity of the free exciton peak is higher by a factor of eight, whereas at higher beam energy the peak at 3.347 eV exhibits almost the same intensity than the free exciton peak. Even for a beam energy of 25 keV we found no indication in the spectra for luminescence from the sapphire subtrate.

At a temperature of T=80 K (Figure 2) the band-edge luminescence peak appears at 3.480 eV for a for a beam energy of 5 keV and shifts to a lower photon energy of 3.466 eV when the beam energy is increased to 25 keV. The spectra also show a donor-acceptor-pair (DAP) at 3.285 eV with its phonon replica. Unlike the near band-edge emission its position is constant when increasing the beam energy. This proves that the fundamental band gap does not change with depth.

The band-edge peak shift is too large to be explained by stress gradients. The strain related peak shift, measured also by low-temperature PL for this sample (not shown here), is about 5-7 meV, as typical for this material [2]. Typically, strain relaxation takes place over a distance of approximately 50 μm from the substrate [8]. We can also rule out the effect of change in excitation density as just a local temperature increase under the electron beam, because the position of the free exciton does not change with   beam current varying over two orders of magnitude. Therefore, the cause of the observed peak-shift is not a change of physical properties with depth.

4.2   Simulation of CL spectra for various beam energies

Recently, it was published that the band-edge of GaN is not as steep as expected for a direct III-V semiconductor [9]. Instead, a pronounced exponential band tail with Urbach energies of 30 meV for GaN and up to 200 meV for the $Al_xGa_{1-x}N$ alloys has been found. This could originate from structural disorder, or could be caused by point defects, alloy fluctuations, or impurities creating shallow defects such as silicon or oxygen.

Next, we simulate CL spectra using a simple model based on the electron energy dissipation of the incident beam and taking into account the effect of internal absorption in GaN.

The exponential absorption tail below the fundamental gap E_g may be described empirically as [10]:

$$\alpha(h\upsilon) = \alpha_0 \exp\left(h\upsilon / E_{Urb}\right), \quad h\upsilon < E_g \qquad (1)$$

with photon energy $h\upsilon$. The Urbach parameter E_{Urb} has units of energy and is assumed to be related to disorder in the material. Using the definition of the effective band gap as the energy $E_{4.8}$ at which the absorption coefficient is equal to $10^{4.8}$ cm^{-1}, we calculate the parameter α_0 for different E_{Urb} assuming $E_g=E_{4.8}=3.420$ eV at T=300 K.

The transmission through a layer of thickness z is given by:

$$I(z) = I_0 \exp(-\alpha z) \qquad (2)$$

The function of electron-hole pair generation vs. depth $\lambda(z)$ is proportional to the energy dissipation of the incident electron beam. We use the empirical relation found by Everhart and Hoff [11]:

$$\lambda(z) = \begin{cases} 1/R\left(0.6 + 6.21(z/R) - 12.4(z/R)^2 + 5.69\,(z/R)^3\right); & 0 \le z < 1.1R \\ 0; & z \le 1.1\,R \end{cases} \qquad (3)$$

where R is the primary electron range. R depends on the beam-energy and the density of the material. Matsukawa et al. [12] give the empirical relation for R (in μm):

$$R = \left(0.052/\rho\right) E_0^{1.75} \qquad (4)$$

with ρ the materials density in g/cm^3 and E_0 the beam energy in keV. Assuming that the minority carrier diffusion length is small compared to the primary electron range, we use Equation (3) to calculate the depth function of the luminescence generation. For the internal, excitonic, near band-edge luminescence L_{int} we assume a gaussian broadening:

$$L_{int}(h\upsilon) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{\left(h\upsilon - E_{exc}\right)^2}{2\sigma^2}\right) \qquad (5)$$

where E_{exc} is the excitonic peak position and σ is the parameter of the gaussian broadening. The measured luminescence L_{ext} is then given by the integral:

$$L_{ext}(h\upsilon) = \int_0^{1.1R} I(z, h\upsilon)\,\lambda(z)\,L_{int}(h\upsilon)\,dz \qquad (6)$$

Figure 3 shows the transmission of GaN calculated using Equation (2) for layers of different thickness. Parameters for the effective band-gap and Urbach energy were taken from recent measurements of optical constants of GaN at room-temperature [9]. For a 1 μm thick layer, the transmission starts to decrease at a photon energy as low as 3.30 eV (Figure 3). This must be compared with the maximum of the energy dissipation as a function of beam energy calculated for GaN using Equation (3) (Figure 4), which corresponds to the depth where the maximum of the generated luminescent light

is. It is seen that, for beam energies around 25 keV, the luminescent light must penetrate a layer more than 1 μm thick. This shows that for luminescent light with near band-edge energy, the transmission considerably effects the CL spectrum, "cutting" the signal on the high energy side of the near band-edge peak. The peak shift could be expected to be strongest for lines with large FWHM in the order of the Urbach energy. Taking this effect into account, the spectra calculated using Equation (6) clearly show a shift of the peak maximum (Figure 5). It also shows, that due to the higher absorption, the peak amplitude is reduced when beam energy is increased. This explains why the peak with lower photon energy becomes stronger for an increasing beam energy at the same time.

In order to compare the measured peak-shift with the simulations, the position of the peak maximum as a function of beam energy is calculated in Figure 6 for different E_{Urb}. The parameter σ for the gaussian broadening was chosen as 25.5 meV, equal to the CL spectra at T=300 K, which gives a FWHM of 60 meV. It is seen that the peak shift observed in our sample corresponds to a Urbach parameter of 30 to 40 meV. This value is in good agreement with optical transmission measurements [9] of samples with a similar structural quality. Thus, we can explain the observed peak-shift quantitatively by taking into account internal absorption.

5 Summary

In conclusion, we explain a shift of the band-edge peak to lower photon energy as the beam energy is increased by internal absorption. This shift is not primarily due to a depth variation of physical properties, such as the fundamental band-gap energy, since the position of the donor-acceptor-pair, measured at T=80 K, is independent of beam energy. We simulate CL spectra and take into account internal absorption using a simple model based on the electron energy dissipation of the incident beam. We compare simulated spectra with the measured band-edge peak positions and estimate an Urbach parameter of 30 to 40 meV for our samples. This value is in good agreement with the 30 meV recently measured by optical transmission for GaN at room temperature.

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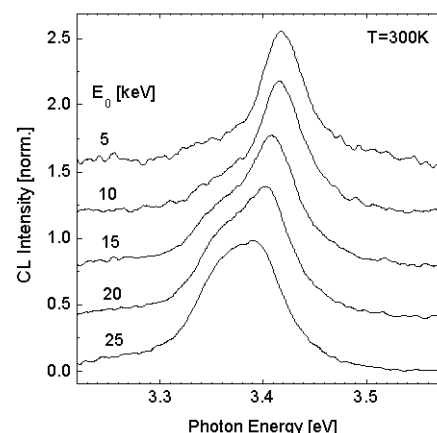
FIGURES

Figure 1. CL spectra for a 2 μm thick GaN thin-film, grown by MOCVD on c-plane sapphire, acquired at T=300 K for a range of electron beam energies. The peak of the free exciton shifts to lower energies as the penetration depth of the beam is increased.
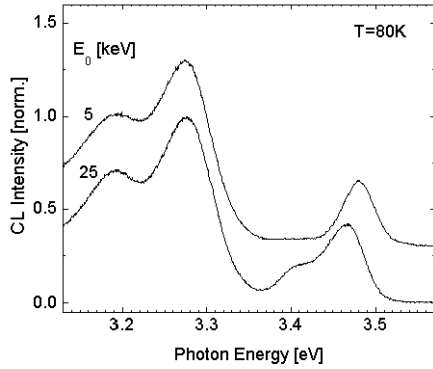
Figure 2. CL spectra for a 2 μm thick GaN thin-film acquired at T=80K for two different beam energies.
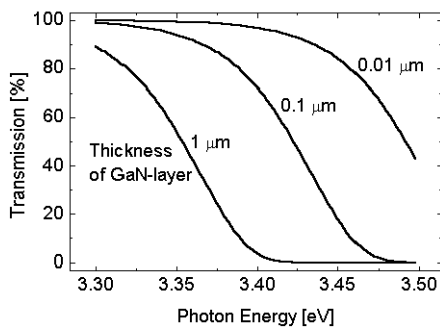

Figure 3. Calculated room temperature transmission at the band-edge of GaN for layers of various thickness. An exponential absorption edge, Urbach energy 30 meV, and an effective band-gap of 3.420 eV are assumed.
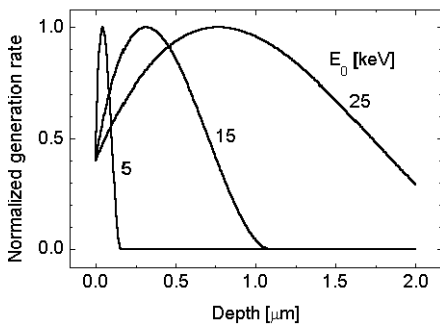

Figure 4. Plots of the normalized carrier generation rate in GaN for various beam energies (Density: ρ=6.1 g/cm^3).
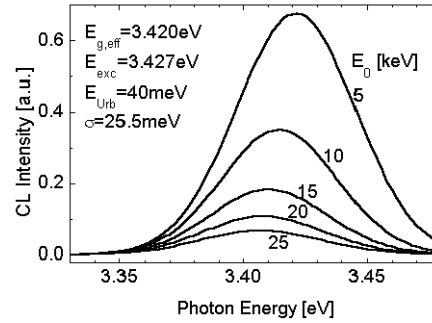

Figure 5. Simulated CL spectra as a function of beam energy. As an effect of internal absorption in GaN the peak maximum shifts to lower energies with higher beam energy. The gaussian broadening parameter σ is chosen to give a linewidth (FWHM) of 60 meV.
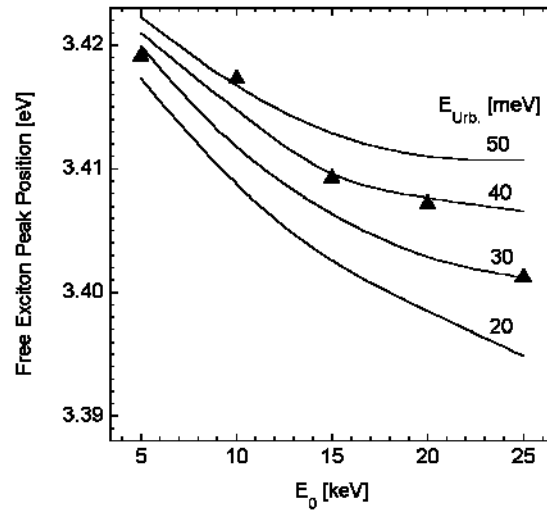

Figure 6. Measured free exciton peak position at T=300 K (triangles) vs. beam energy compared with simulated peak positions (solid lines) for various Urbach tail energies (Parameters: E_{exc}=3.427 eV, σ=25.5 meV). The peak-shift depends strongly on the shape of the band tail.

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