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Near band-edge optical properties of cubic GaN with and without carbon doping

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Abstract

We report the results of studying the optical properties of cubic GaN thin films with photoluminescence and photoluminescence excitation spectroscopies. The films are deposited by plasma-assisted molecular beam epitaxy on GaAs (001) substrates, with and without intentional doping with carbon atoms (p-type doping). The evolution of the optical spectra of the C-doped samples is consistent with a picture in which carbon enters into N-vacancies at low concentrations, producing a marked improvement in the crystalline properties of the material. At higher concentrations it begins to form complexes, possibly due to interstitial occupation. The temperature dependence on the absorption edge of the doped material is also measured and is analyzed with standard theoretical models.

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1. Introduction

The fabrication of the first c-InGaN/GaN double-heterostructure LED grown by MOCVD has been recently reported [1]. Contrary to their hexagonal counterparts, the cubic structures can be grown free from modulation due to spontaneous polarization and strain-induced piezoelectric fields. Thus, the spatial separation of the carriers wave function, induced by the quantum-confined Stark effect in the hexagonal phase, is avoided in the cubic phase. For this reason the cubic polytype nitride-based quantum wells are expected to have increased optical recombination efficiency. Hence, the growth and characterization of high-quality c-GaN epitaxial layers are essential first step on the road to high-performance devices fabricated with this material. In addition, for the fabrication of devices with this material, it is essential to be able to introduce p- and n-type doping in a controlled manner. This involves introducing dopant impurities, which produce shallow acceptor or donor levels. Understanding how these

impurities enter into the GaN lattice is of fundamental importance for achieving useful doping.

In the present work, we report the results of a study of the optical properties of cubic GaN thin films, deposited by plasma-assisted molecular beam epitaxy on GaAs (001) substrates, with and without intentional doping with carbon atoms (p-type doping). We used photoluminescence (PL) and photoluminescence excitation spectroscopy (PLE) to study the spectral region near the fundamental absorption edge of these samples. We observe a clear step-like absorption edge, resulting from the merging of the free exciton with the continuum. Quantitative values for the absorption edge energy and lifetime broadening are obtained. The temperature dependence on the absorption edge of the doped material is also measured and is analyzed with standard theoretical models. The evolution of the optical spectra of C-doped samples as the concentration of the dopant increases is consistent with a picture in which carbon enters into N-vacancies at low concentrations, producing a marked improvement in the crystalline properties of the material. At higher concentrations, it begins to form complexes, possibly due to interstitial occupation.

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2. Experimental

Cubic GaN films were grown by rf-plasma assisted MBE on semi-insulating (001) GaAs substrates at a temperature of 720 °C. The growth rate was of 0.07 $\mu\text{m}/\text{h}$ and the total thickness of each film was approximately 1 μm . Carbon doping was achieved, as explained in detail in Ref. [2], by electron beam evaporation of a graphite rod, with the e-beam power maintained constant between 0 and 400 W during the growth. The C-flux was calibrated by growing C-doped GaAs in the same manner and assuming the same sticking coefficient for C on GaAs and GaN. Secondary ion mass spectroscopy was used in some samples to determine the carbon concentration [2]. The samples used in our experiment are labeled A through H in order of increasing carbon content as listed in Table 1.

Both PL and PLE spectra were excited with an air-cooled 1000 W Xe lamp filtered by a 1.0 m SPEX monochromator with a 1200 groove/mm grating. The monochromatic light was focused onto the sample, contained in an Air Products cold finger cryostat in which temperature can be varied continuously from $T = 10$ K to room temperature. Emitted light was focused into a double monochromator with a Ga–In–As photomultiplier tube. Quartz lenses were used both for excitation and collection of emitted radiation.

3. Results and discussion

PL and PLE spectra of the undoped sample (sample A in Table 1) are displayed in Fig. 1. The PL spectrum obtained here by low power density excitation with a filtered Xe-arc is entirely similar to the spectra obtained by excitation with laser sources reported by the authors of Ref. [3]. Two clear narrow structures characterize this spectrum, attributed to acceptor–donor transitions (3.15 eV) and bound exciton (3.26 eV), respectively. In the PLE experiment, best results are obtained when centering the analyzing spectrometer at the PL peak at 2.86 eV. The resulting PLE spectrum mimics

Table 1

List of samples used in our experiments with their thickness and ordered according to their carbon content

Sample	Thickness (nm)	e-Beam power (W)	[C]
A	185	0	0
B	1030	70	2×10^{17}
C	1035	90	2.5×10^{17}
D	1121	150	4×10^{17}
E	728	200	8×10^{17}
F	676	280	3×10^{18}
G	677	350	1.5×10^{19}
H	647	400	2×10^{20}

The amount of carbon incorporated ([C]) is estimated from the evaporating e-beam power used during growth.

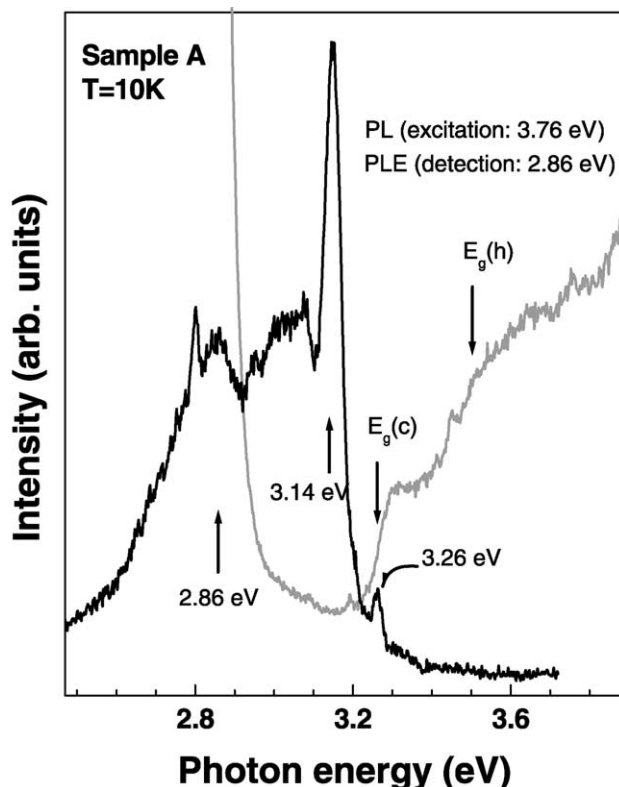


Fig. 1. Low temperature PL and PLE spectra of sample A (Table 1). Arrows indicate structures in both spectra.

the absorption spectra and closely resembles two broadened step functions located at different photon energies. This lineshape is characteristic of a M_0 singularity with an exciton, which is broad enough to merge with the continuum [4]. Fitting this spectrum with two broadened step functions, we obtain values for the photon energy of the two absorption edges (E_g), as well as for their broadening parameters, Γ (full width at half maximum, FWHM). Arrows in Fig. 1 indicate the location of these two critical points in the absorption, designated as $E_g(c)$ and $E_g(h)$, respectively, in order of increasing photon energy. We attribute the first critical point ($E_g(c) = 3.26$ eV, $\Gamma = 50$ meV) to the absorption edge of cubic GaN and the second one ($E_g(h) = 3.5$ eV, $\Gamma = 0.2$ eV) to the absorption edge of hexagonal inclusions present in the material. The very large width ($\Gamma = 50$ meV) in the absorption edge of the cubic material is attributable to strain due to sample imperfections. This interpretation is reinforced by the fact that this width changes very little from 10 K to room temperature [5].

The low temperature PL spectra of two samples with different C content (samples F and G, listed in Table 1), as well as that of sample A (undoped), are shown in Fig. 2. A detailed discussion on the relationship between carbon content and the PL spectra from carbon-doped c-GaN samples can be found in Ref. [2]. Here, we shall

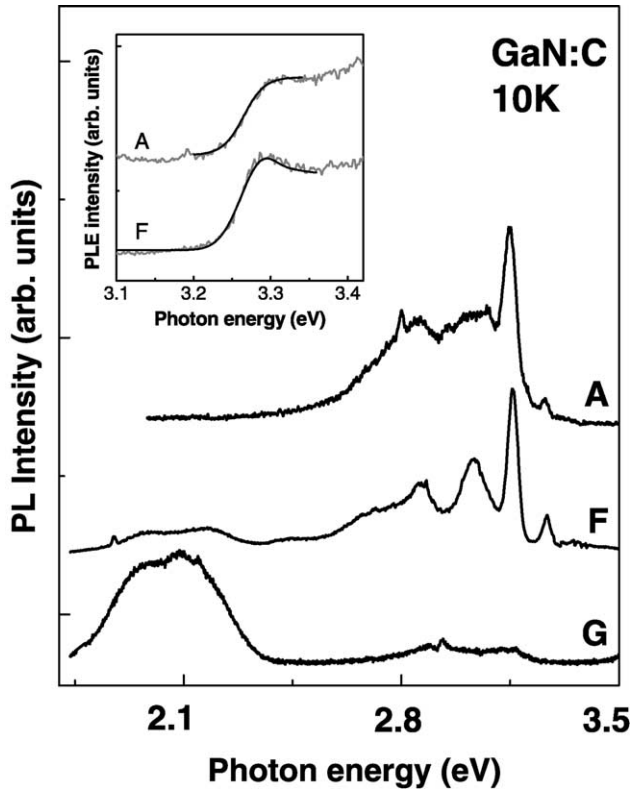


Fig. 2. PL spectra of cubic GaN samples with and without carbon-doping (Table 1). Inset shows PLE spectra of samples A (undoped) and F (carbon-doped).

concentrate our discussion around two features of these spectra. The first is composed of two sharp peaks around 3.15 and 3.26 eV, respectively. The first peak is attributed to donor–acceptor (D^0-A^0) transitions and the second to recombination from the bound exciton. These peaks also appear in the PL spectra of samples of cubic GaN not intentionally doped [6] or n-doped [2]. In these samples there is always a residual acceptor concentration, attributed to the large dislocation density ($\sim 10^{11} \text{ cm}^{-2}$) present in the films, which are involved in the D^0-A^0 transition at 3.15 eV [2,6]. The second feature appears only in the PL spectra of samples with higher carbon concentration (samples F–H in Table 1). This feature is a complex band around 2.1 eV, which grows in intensity as the C content increases and eventually dominates the spectrum for the most heavily doped samples (bottom curve in Fig. 2). This line is attributed by the author of Ref. [2] to the formation of a compensating dicarbon split-interstitial center, i.e. a complex formed by a carbon atom occupying a N-site and a second C-atom in an interstitial position. The increase in the intensity of this band coincides with a decrease in the intensities of the bands at 3.15 and 3.26 eV. In fact, upon increasing the C-concentration, the intensity of the original D^0-A^0 transition decreases and all but disappears for the most highly doped sample

(compare the curves for samples F and G in Fig. 2). In principle, this can be caused by the disappearance of the donor levels resulting from heavy p-type doping. On the other hand, this is also consistent with the reduction of the lattice distortions provoked by the N-vacancies. Since these distortions are thought to be responsible for the donor levels involved in the 3.15 eV transition, the reduction in their number would result in the observed decrease in intensity of this line.

PLE spectra of samples A and F, around the absorption edge region, are shown in the inset of Fig. 2. These spectra were obtained by centering the analyzing spectrometer at PL peaks at 2.86 eV for sample A and around the C-complex band at 2.1 eV for the carbon-doped samples. As previously discussed, for sample A the absorption edge resembles a broadened step function, a lineshape characteristic of a M_0 singularity with an exciton that is broad enough to merge with the continuum. Fitting this spectrum with a broadened step function (see the inset in Fig. 2), we obtain for the photon energy of the absorption edge and broadening parameter (FWHM) the values: $E_g = 3.26$ and $\Gamma = 50$ meV, respectively [5]. The absorption edge profile of sample F, however, has the exciton well resolved from the continuum. This profile is well fitted with the combination of a Gaussian (exciton absorption) and a broadened step function (continuum). The result of this procedure is an excitonic line ($E_{\text{exc}} = 3.289$ eV, $\Gamma = 23$ meV) separated from the absorption edge by 32 meV. The same is true for all carbon-doped samples, with the exciton resolution improving as carbon concentration increases up to sample F and then becoming broader as carbon concentration increases further (not shown). The above discussion shows that carbon incorporation clearly improves the crystalline quality, allowing for a better resolution of the exciton from the continuum, up to the point when carbon begins to incorporate at non-substitutional sites and crystalline quality again begins to deteriorate. However, the crystalline quality of C-doped samples remains better than that of the undoped ones, even for the samples grown with the highest carbon concentration, as evidenced by the sharpness of their absorption edges.

Finally, PL and PLE experiments were performed on the carbon-doped sample exhibiting the best crystalline quality (sample F) as a function of temperature in the range from 10 to 300 K. Results for the absorption edge of the cubic material are displayed in Fig. 3. Here, we can observe qualitatively a decrease of E_g and an increase in Γ as temperature increases. By fitting these spectra in the manner previously explained, we can obtain these parameters as a function of temperature. The values of E_g vs T are displayed in Fig. 4 as open squares. The peak energy of the main exciton, obtained from the PL spectrum, as a function of temperature is shown in this figure as open circles. Continuous lines represent fittings of E_g vs T using

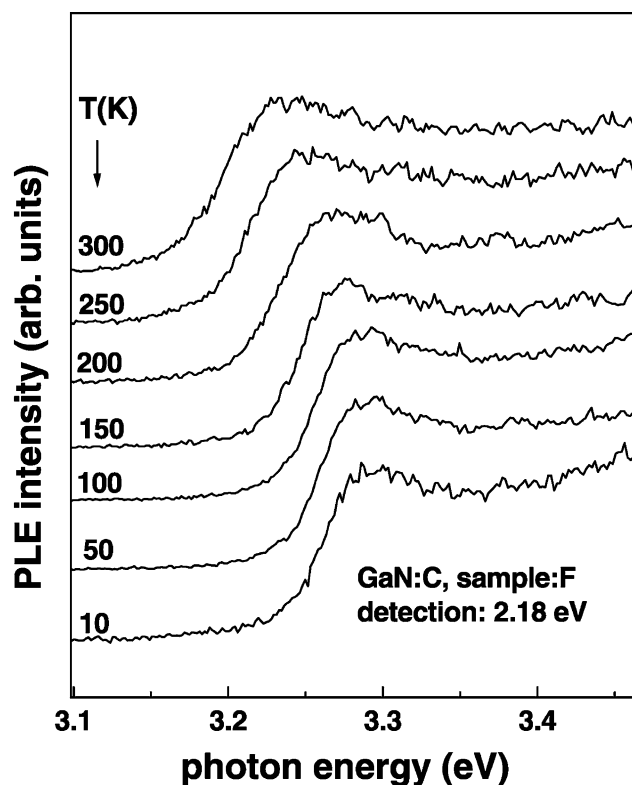


Fig. 3. Absorption edge of sample F (Table 1) determined from PLE measurements performed at different temperatures.

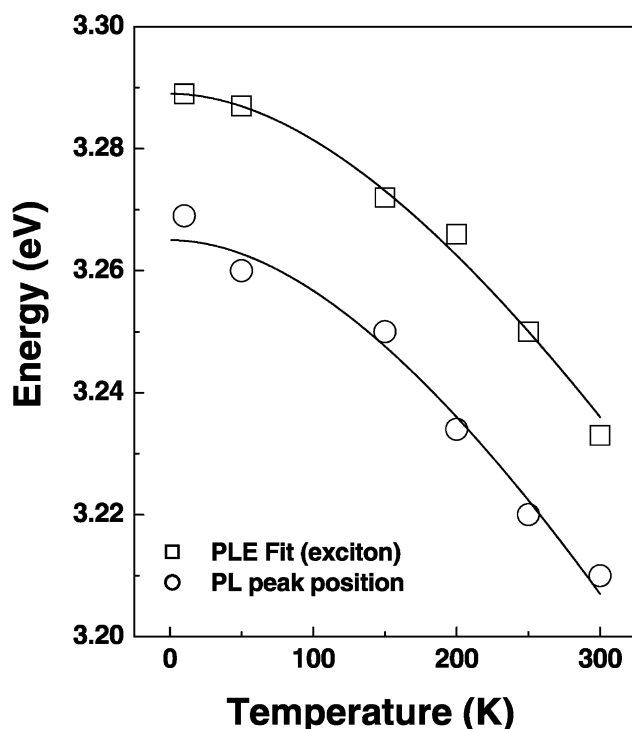


Fig. 4. Temperature dependence of the critical (Table 1). Dots (squares) are experimental data and solid lines are fitted to Eq. (1).

Varshni's formula [7]:

$$E_g(T) = E_g(0) - \alpha T^2 / (\beta + T) \quad (1)$$

For the exciton energy obtained from fitting the PLE spectra, we obtain $E_g(0) = 3.289 \pm 0.001$ eV and $\alpha = (5.5 \pm 0.2) \times 10^{-4}$ eV/K for $\beta = 600$ K. These values are consonant with those obtained for c-GaN deposited on MgO substrates [8] and results for our undoped c-GaN samples deposited on GaAs (100) substrates [9]. The PL peak position is fitted with a very similar value of α ($\alpha = 5.8 \times 10^{-4}$ eV/K) and a value of $E_g(0)$ downshifted from the previous one by 24 meV. Finally, the linewidth of the exciton line in the absorption edge varies from 13 meV at 10 K to 16 meV at room temperature. This variation of about 20% is too small, when compared to other III–V materials of good crystalline quality. This points to the presence of residual strain due to sample imperfections, which is present even in our best quality samples.

4. Summary and conclusions

We have presented experimental optical data that give a strong indication of the lattice sites occupied by carbon during growth of carbon-doped GaN by rf-plasma assisted MBE on semi-insulating (001) GaAs. The resulting picture for the carbon incorporation into the c-GaN lattice is the C-atoms initially enter the sites of N-vacancies in the native material, thus improving its crystalline quality. The higher the C concentration, the better the crystallinity of the sample, up to a critical power (200 W in our system). At higher powers, C-atoms begin to incorporate non-substitutionally and form complexes, degrading the crystalline quality once more. Although increasing the e-beam power above 200 W degraded the crystalline structure of the samples, all C-doped samples, even those grown with the maximum e-beam power (400 W), have a better crystalline quality than undoped samples. The temperature dependence of the absorption edge, measured in the sample with best crystalline quality (sample F), is comparable to the one obtained for undoped samples by ourselves and other authors. The temperature dependence of the linewidth, however, indicates the presence of residual strain even in this sample.

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