Optical transitions in cubic GaN investigated by spatially resolved cathodoluminescence

J. Menniger, U. Jahn, O. Brandt, H. Yang, and K. Ploog
Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, D-10117 Berlin, Germany

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Spatially resolved cathodoluminescence (CL) spectroscopy in connection with scanning electron microscopy performed on cubic (c) GaN between 5 and 300 K reveals that at low temperatures the CL spectra of c-GaN single crystals consist of four well-separated lines. The two lines highest in energy were previously identified as excitonic and donor-acceptor transitions, respectively. Here, we show that the lines lowest in energy are due to an additional free-to-bound transition, involving an impurity different from those related to the donor-acceptor transition, and its phonon replica. The CL spectra of c-GaN layers, while being rather broad, are composed of these four lines. Moreover, at 300 K the spectra of the layers and of the crystals are both dominated by the excitonic transition and closely resemble each other. © *1996 American Institute of Physics.* [S0003-6951(96)02732-5]

Under equilibrium conditions, GaN crystallizes in the hexagonal structure. In the last few years, however, growth conditions suitable for the preparation of metastable cubic (c) GaN layers on various substrates were found.[1–5] With regard to the optical properties of this cubic modification the interpretations of the respective radiative transitions given by different authors are inconsistent with each other. Strite *et al.*[1] investigated c-GaN grown by molecular beam epitaxy (MBE) on a GaAs(001) substrate by cathodoluminescence (CL). The authors obtained CL spectra at 4 K with distinct lines at 3.269 eV (α), 3.190 eV (β), and 3.095 eV (γ), as well as a much weaker feature at 3.52 eV. They tentatively assigned α and β to impurity related transitions—β was interpreted as donor-acceptor ($D°$, $A°$) pair transition—and the feature at 3.52 eV to the band gap emission of c-GaN. Okumura *et al.*[4] reported similar lines in photoluminescence (PL) spectra of c-GaN layers grown by MBE on a SiC substrate. These authors, however, assigned line α to the excitonic recombination in c-GaN. Liu *et al.*[3] presented a PL spectrum of a c-GaN layer grown by MBE on a β-SiC coated Si substrate, which was dominated by a rather broad PL band with a peak energy of 3.23 eV at 7.5 K. However, the authors did not comment on the origin of this transition.

These discrepancies are presumably caused by inclusions of the hexagonal (h) GaN phase, high densities of planar defects and impurities as well as residual strain. Obviously, the structural properties of the samples largely influence their optical properties, and hence must be taken into account for interpreting luminescence spectra. Recently, we have reported on spatially resolved CL spectra and spectrally resolved CL images of hexagonal and cubic micron-size GaN single crystals grown by MBE on a GaAs(001) substrate.[6] The exciton (free: 3.272 eV, bound: 3.263 eV) and the ($D°$, $A°$)-pair (3.150 eV) transitions of c-GaN have been identified. CL lines at energy positions below the ($D°$, $A°$)-pair line are weak in these large crystals, but become dominant for c-GaN layers. The aim of this article is to identify these latter transitions by temperature (T) dependent CL taken from small c-GaN crystals and from thin c-GaN layers. Furthermore, CL spectra of c-GaN exhibiting different surface morphologies are compared to each other.

We have investigated four c-GaN samples (A, B, C, and D) fabricated by solid-source molecular beam epitaxy (MBE) on GaAs(001) substrates, employing a DC plasma discharge source to dissociate molecular N_2 and to form N_2 ions. Growth of GaN is initiated at 620–680 °C under nearly stoichiometric conditions using a slow growth rate (0.05 ML/s). The growth procedure resulting in microcrystals on top of the GaN layers is described elsewhere in detail.[6] Samples A and B contain randomly distributed stacks of 0.1–1μm large GaN single crystals. Samples C and D consist of c-GaN layers which are free of these crystals and are 185 and 250 nm thick, respectively. The main structural difference between these samples is that the density of planar defects, such as stacking faults and microtwins, is very high for c-GaN layers of this small thickness, but almost zero for the c-GaN crystals.[7]

The CL experiments are carried out in a scanning electron microscope (DSM 962) equipped with an Oxford Mono-CL and He cooling stage system providing continuous temperature control ranging from 5 to 300 K. The electron beam energy amounts to 5–8 keV and the current is about 1 nA. A grating monochromator and a cooled photomultiplier are used in conjunction with conventional photon counting technique to disperse and detect the CL, respectively. The surface morphology of the GaN samples is monitored by secondary electron (SE) microscopy.

The investigated c-GaN crystals and layers exhibit different surface morphologies, which are illustrated in Figs. 1(a)–(d) by SE micrographs. Figures 1(a), (b), (c), and (d) correspond to the samples A, B, C, and D, respectively. While the size of the well separated c-crystal in Fig. 1(a) (arrow) amounts to about 1 μm, the crystals in (b) are smaller and not well separated. The facets of the crystals are rather smooth, whereas the surfaces of the c-GaN layers exhibit a certain roughness with sharp ridges partly arranged in rhombic form [(cf. Fig. 1(d)]. Figure 2 shows CL spectra A, B, C, and D obtained from the respective samples at 5 K. The CL spectrum A of Fig. 2 originating from the crystal marked in Fig. 1(a) is dominated by the lines α and β, which were previously identified as exciton and ($D°$, $A°$)-pair transition of c-GaN, respectively.[6] In smaller crystals and in

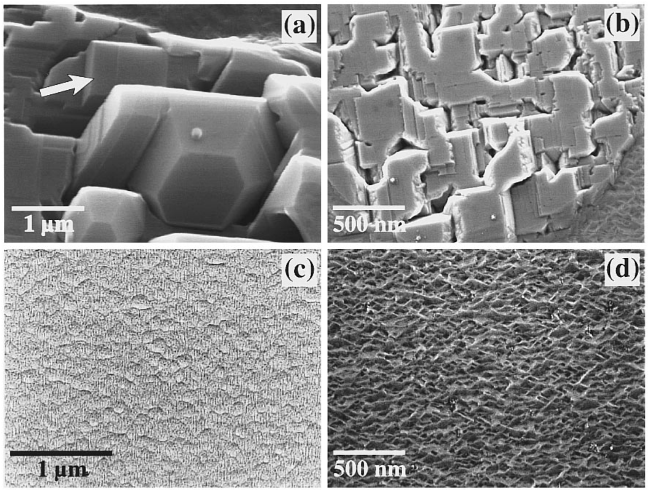

FIG. 1. Secondary electron micrographs of c-GaN crystals and layers with (a) to (d) corresponding to samples A to D, respectively.

GaN layers, the excitonic transition is suppressed at low temperatures (spectra B–D), and lines γ (3.08 eV) and δ (2.99 eV) contribute increasingly to the spectrum. Moreover, for c-GaN layers the CL lines become broader and are spectrally not resolved for sample D. However, it is obvious that the four CL lines α, β, γ, and δ are characteristic for the near-band gap luminescence of c-GaN, since α, β, and γ were also found by other authors even for layers grown on different substrates.[1,4]

For the discussion of the CL lines γ and δ, we focus here on the CL spectra of small GaN crystals (sample B). Since the energy spacing between the spectral positions of β and γ amounts to about 90 meV, it is tempting to assign γ to a LO phonon replica of the ($D°$, $A°$)-pair transition (line β). However, as can be clearly seen from the T-dependence of the CL

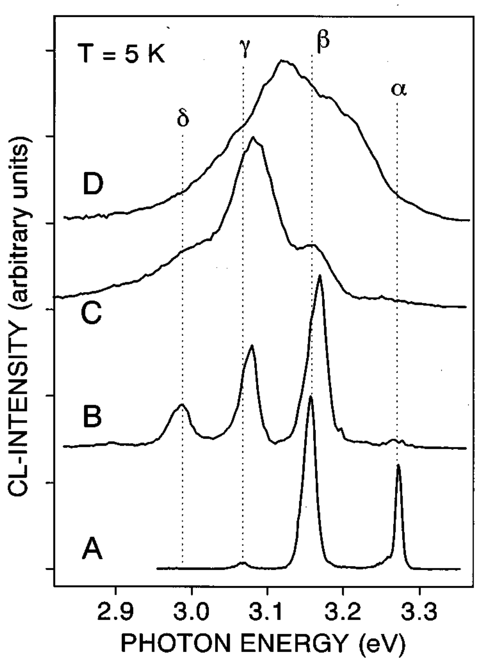

FIG. 2. Cathodoluminescence spectra of c-GaN crystals and layers. Spectra A to D correspond to the respective samples described in the text.

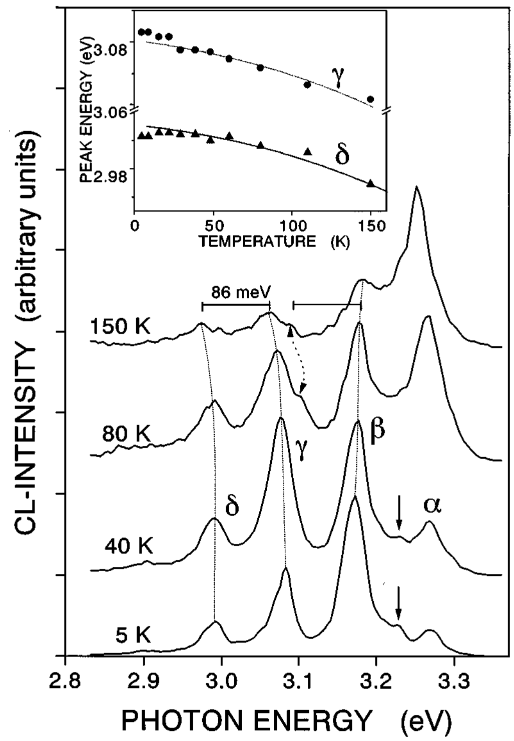

FIG. 3. Cathodoluminescence spectra of c-GaN crystals (sample B) at different temperatures. The bars mark the energy spacing of the phonon replica in c-GaN.[6] Inset: Temperature dependence of the peak energy of the CL lines δ and γg. The solid lines mark the rigidly shifted temperature dependence of the band-gap energy of c-GaN according to Ref. 12.

spectra in Fig. 3, an opposite shift of the peak positions of γ and β is observed with increasing T, indicating different origins of the respective optical transitions. While β shifts towards higher photon energies as expected for a ($D°$, $A°$)-pair transition [cf. Fig. 4(a) of Ref. 6], γ shifts towards lower energies. The detailed T-dependence of the spectral positions of λ and δ is shown in the inset of Fig. 3. For both CL lines, we find a continuous decrease of the peak energy with increasing T following the shift of the band gap. Con-

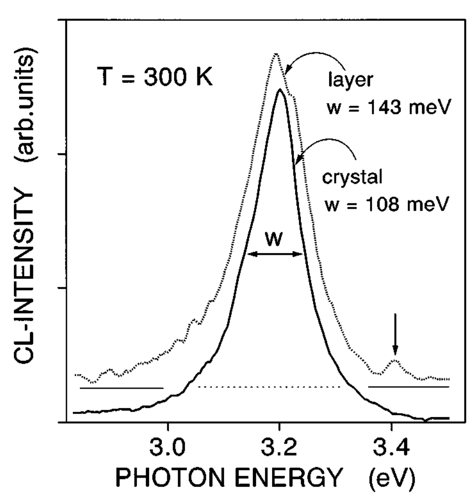

FIG. 4. Cathodoluminescence spectra of a c-GaN crystal (sample B) and of a c-GaN layer (sample D) at 300 K. The arrow at about 3.4 eV marks the contribution from inclusions of h-GaN in the layer.

sequently, γ cannot be assigned to a phonon replica of the ($D°$, $A°$)-pair transition, but to an additional free-to-bound transition (X,x) involving a level which is located about 0.22 eV deep in the band gap. However, at higher temperatures (80 and 150 K) γ exhibits a high-energy shoulder (dotted arrows) being separated from β by the LO phonon energy (bars in the top spectrum of Fig. 3). Consequently, γ consists of two lines, but its intensity is dominated by the (X,x) transition. With regard to δ, we find that the energy separation between γ and δ is identical to the LO phonon energy. Thus, δ is indeed a LO phonon replica of γ, as confirmed also by the T-dependence of the δ peak position following that of γ (cf. inset of Fig. 3).

We next discuss the nature of the (X,x) transition in relation to results obtained from hexagonal GaN. Dingle *et al.*[8] and Monemar and Lagerstedt[9] assigned states exhibiting binding energies E_A of 213 and 225 meV, respectively, to the shallowest acceptor level in h-GaN, which contributes to the commonly observed ($D°$, $A°$)-pair emission. A similar acceptor level ($E_A \approx 190$ meV) is involved in a model proposed by Glaser *et al.*[10] to explain the origin of the so-called ''yellow luminescence'' of h-GaN at about 2.2 eV. Since such an acceptor level seems to be a universal feature of h-GaN occuring independently of intentional doping, it must be related to either an intrinsic defect (such as the Ga vacancy[11]) or to inevitable environmental contaminations during growth such as C.[10] It is thus likely that the (X,x) transition involves a second shallow acceptor state ($E_x \approx 220$ meV) in c-GaN, perhaps due to the same defect as in h-GaN, in addition to the shallow acceptor level ($E_A \approx 90$ meV) which contributes to the ($D°$, $A°$)-pair line.[6]

The T-dependence of the CL spectra in Fig. 3 shows that the defect and/or impurity related lines disappear with increasing T while the excitonic luminescence survives. The same behavior is observed for CL spectra of c-GaN layers confirming our assumption that the broad CL spectrum for sample D of Fig. 2 consists of the same lines as the spectra obtained from the crystals. Figure 4 shows the spectra of a c-GaN layer (sample D) and of a crystal (sample B) obtained at 300 K. Both spectra are dominated by the excitonic transition and closely resemble each other, though the CL spectrum of the layer is about 30% broader than that of the crystal. The weak CL peak at 3.408 eV in the spectrum obtained from the cubic GaN layer (arrow in Fig. 4) represents the exciton transition of h-GaN and is thus due to small inclusions of this phase in the predominantly cubic layer.

In summary, we conclude that at low temperature the luminescence spectra of cubic GaN vary considerably with the morphology and thus the density of structural defects. While CL spectra of micron-size single crystals are dominated by the exciton and ($D°$, $A°$)-pair lines, spectra of smaller crystals and of cubic GaN layers are governed by defect related transitions. Besides the exciton and ($D°$, $A°$)-pair lines, we find at 3.08 and 2.99 eV CL lines which are related to a defect level and its phonon replica, respectively. The line widths increase with decreasing crystal size. For cubic GaN layers, the CL spectrum reduces to a broad band which is, however, composed of the lines found in the crystals. At 300 K, the spectra of the layers and of the crystals are both dominated by the excitonic transition and closely resemble each other.

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