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Characterization of free standing GaN grown by HVPE on a $LiAlO_2$ substrate

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A 230 μm thick free standing GaN layer has been grown on a $LiAlO_2$ substrate by hydride vapor phase epitaxy, with the separation of the layer from the substrate occuring spontaneously during cooling down after growth. A strong green luminescence band is observed from the top surface, while from the bottom surface, strong blue and red bands are seen in photoluminescence (PL). The evolution of these luminescence bands with layer thickness was monitored by cross-sectional cathodoluminescence (CL). PL and CL measurements indicate that the defect structure changes with growing layer thickness.

1 Introduction

GaN is currently the most important material for short-wavelength light emitters and high-power, high-temperature RF-devices. Due to the lack of GaN substrates, most GaN layers are grown on foreign substrates, mainly sapphire and SiC, which introduce significant strain and a high density of structural defects compromising device performance. Growth of GaN layers on GaN substrates thus is highly desirable. Hydride vapor phase epitaxy (HVPE) currently is the method of choice for the growth of very thick GaN layers, which can be used as substrates for further homoepitaxy. HVPE growth of thick GaN layers has been demonstrated on sapphire substrates, but the separation from the substrates requires laser-induced lift-off as an additional process step [1, 2]. The lattice mismatch between $LiAlO_2$ and GaN is only 1.4%, which is much lower than the 16% mismatch of GaN on sapphire [3]. Recently, free standing GaN layers have been achieved using $LiAlO_2$ as substrate material with the separation of the layer from the substrate occurring spontaneously [3].

Understanding the growth mechanism and monitoring the changes of the material quality with growth conditions and layer thickness are very important for achieving high quality GaN substrates for device applications. In this paper, we report on the characterization of a 230 μm thick free standing 2″ GaN layer by different techniques, including steady-state photoluminescence (PL), time-resolved PL, cathodoluminescence (CL), and secondary ion mass spectrometry (SIMS).

2 Experimental details

A 2″ diameter GaN layer about 230 μm thick was grown in a horizontal AIX-HVPE quartz reactor on a (100) oriented $LiAlO_2$ substrate. A detailed description of the reactor can be found elsewhere [4]. After nitridation of the substrate under NH_3 in a N_2/H_2 atmosphere, a low-temperature nucleation layer was grown at about 600 °C with NH_3 and Ga (transported by HCl) at a V/III ratio of 50. Subsequently, the

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substrate was heated up close to 1000 °C. After recrystallization for about 2 minutes, about 10 μm were grown at a rate of ~50 μm/h and a V/III ratio around 20 followed by ~220 μm grown at 1010 °C and a rate of 150–200 μm/h with a V/III ratio of 7. During the cooling-down process after growth the GaN layer self-separated from the substrate.

PL experiments were performed at temperatures between 10 K and 300 K using a 325 nm He–Cd laser as excitation source. The excitation intensity was varied by a neutral density filter. CL measurements were carried out at 80 K using a JSM-840A scanning electron microscope and an OXFORD monoCL system. A pulsed nitrogen laser (337 nm) was used for the time-resolved PL measurements at room temperature. The transient PL spectra were acquired using a CCD camera.

3 Results and discussion

Curve (a) in Fig. 1 shows the 10 K PL spectrum taken from the top surface with an excitation density of about 5 W/cm^2. The sharp lines near the band edge dominate the spectrum. A broad green luminescence band (centered near 2.43 eV) is also observed. The inset of Fig. 1 expands the edge luminescence bands of curve (a). The sharp lines at 3.479 eV, 3.472 eV and 3.455 eV are assigned to the free A exciton (FX_A), neutral donor bound exciton (D^0, X), and neutral acceptor bound exciton (A^0, X), respectively. The two groups of lines at lower energies near 3.38 eV and 3.29 eV are the 1LO- and 2LO-phonon replicas of the features at higher energies. The assignment of the edge luminescence bands is supported by temperature-dependent PL measurements performed in the energy region from 3.2 to 3.5 eV from 10 K to 150 K (not shown here). Using the transition energy of the FX_A at 10 K, the strain present in the top surface is estimated to be negligible [5]. The green band around 2.43 eV has been suggested to stem from a gallium vacancy and oxygen donor (V_{Ga}–O_N) complex [6–8]. Curve (b) in Fig. 1 is a spectrum taken from the bottom surface at 10 K. It shows three bands, the excitonic emission at 3.465 eV, a blue band at

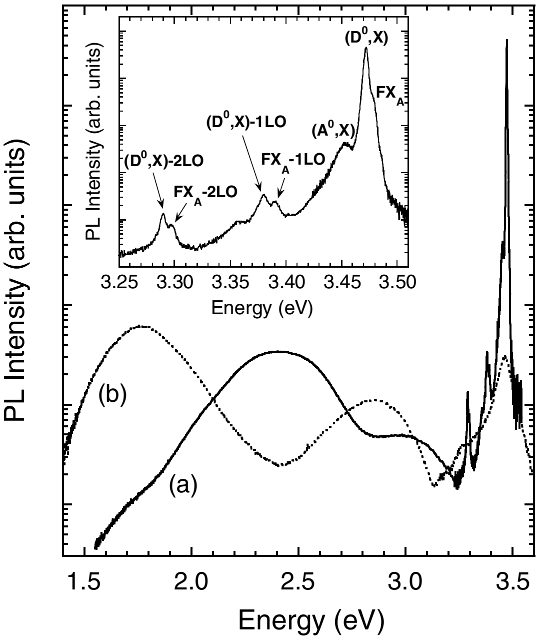

Fig. 1 PL spectra taken at 10 K from the two surfaces of the free standing layer. (a) Top surface (solid line) and (b) bottom surface (dotted line).

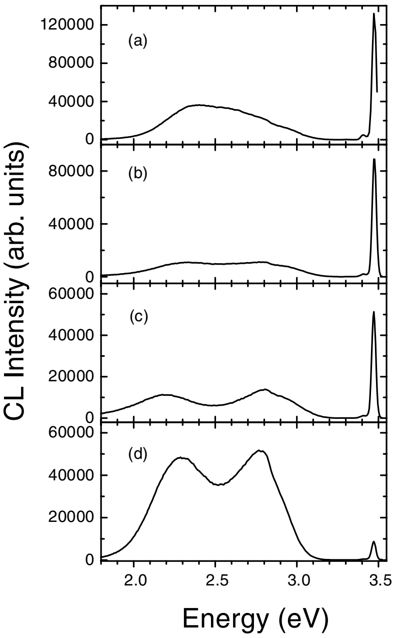

Fig. 2 Cross-sectional CL measurements at 80 K at four different positions along the growth direction. Distances to the bottom surface are about (a) 210 μm, (b) 160 μm, (c) 60 μm, and (d) 20 μm.

about 2.86 eV, and a strong red band at about 1.78 eV. The narrower and more intense excitonic emissions from the top surface indicate better material quality than near the bottom surface. This is consistent with the CL images, which show that the top surface has a reduced density of structural defects.

As demonstrated in Fig. 1, drastic changes in the PL emission band were found from the top surface to the bottom surface. To get some insight into the evolution of the luminescence bands, cross-sectional CL measurements were performed at 80 K. The results are presented in Fig. 2. Curves (a) to (d) are taken from 4 different positions starting near the top surface (a) and ending near the bottom surface (d). Figure 2 illustrates that the intensity of the excitonic emission increases with growing layer thickness, indicating the improving material quality. Curve (a) is similar in shape to the PL spectrum from the top surface. Although curve (d) is taken from the region close to the bottom surface, it shows the blue band and the yellow band, not the red band at 1.78 eV. The yellow band has been correlated with V_{Ga}–O_N complex [9, 10].

PL and CL measurements suggest that the defect structures vary during growth. At the bottom surface, strong blue and red bands were observed, but no V_{Ga}–O_N related yellow band. The blue band has been correlated with carbon impurity and assigned to donor-acceptor pair transition involving the deep C_{Ga} donor and the shallow C_N acceptor [11, 12]. Recently, we have shown that the 1.78 eV red band at 10 K, which shifts to 1.9 eV at room temperature, is also related to carbon impurities [13]. This is supported by the SIMS results, which revealed very high concentrations of C and O impurities (both at about 10^{19} cm^{-3}) present in the bottom region. Their concentrations are significantly reduced to about 10^{17} cm^{-3} near the top surface. The absence of the yellow band can be explained by the high concentration of the substitutional C on Ga site, which reduces the V_{Ga} concentration. Hence, even with a high O concentration, no yellow band is observed. With the layer growing thicker, the C concentration decreases and the C-related blue band becomes weaker. Meanwhile, the V_{Ga} concentration increases and the yellow band is enhanced. By reaching the top surface, the green luminescence is dominant.

To study the properties of the deep level emission, transient PL experiments were performed at room temperature from the top surface. The results are shown in Fig. 3. When the delay time is short (curves (a) and (b)), the observed band is the green band centered near 2.43 eV. After a long-delay time (1 ms), the spectrum shifts to the yellow band. The peak shifts further to the red region after 4 ms delay (curve e). Similar results have been observed by Reshchikov et al. [8]. They observed the change from the green band to the yellow band after 1 ms delay time. However, they did not measure delay times longer than 1 ms. We believe that the defects responsible for the yellow and red bands are present at the top surface, but with much lower concentrations than that responsible for the green band. Moreover, because of the longer lifetimes of the yellow and red bands than that of the green band, they are easier to saturate. At short delay time, only the green band is observed. After longer delay time, the green band is quenched. We are able to resolve the yellow and red bands, but the intensities are much weaker compared to the initial intensity of the green band. The very weak red band in the top surface is also consistent with the assignment of it to carbon impurity, because the C concentration is very low (near the detection limit).

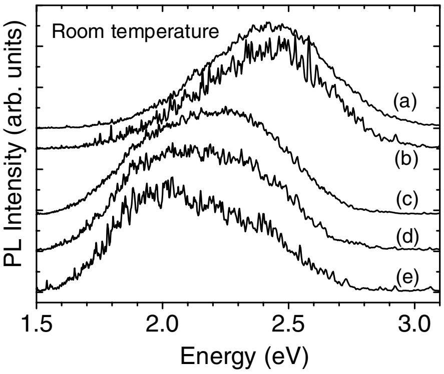

Fig. 3 Transient PL spectra from the top surface for time-delays of (a) 500 ns, (b) 50 µs, (c) 1 ms, (d) 2 ms, and (e) 4 ms. The spectra have been normalized and then vertically shifted for clarity.

We also studied the excitation power dependence and temperature dependence of the green emission from the top surface. The peak and shape of the green band do not change with temperature (from 10 K to 300 K) and excitation intensity, which is varied by more than 4 orders (from 5 W/cm^2 to 0.2 mW/cm^2). Different behaviors of the green emission band have been observed by Reshchikov et al. [6, 7]. They observed a rapid shift from the green band to the yellow band when reducing the excitation intensity from 10 mW/cm^2 to 1 mW/cm^2 and attributed the green and yellow to two charge states of the same impurity (V_{Ga}–O_N complex). Our data suggest that the green band and yellow band are related to two different defects, since the change from the green band to the yellow band has not been observed in our sample for a wider range of excitation intensities. The yellow band is related to V_{Ga}–O_N complex [9, 10]. However, the defect structure responsible for the green band is unclear.

4 Summary

A thick free standing GaN layer was characterized by a variety of experimental methods. Changes of the deep level emission bands with growing thickness were monitored by PL and cross-sectional CL. Our data suggest that green band and yellow band are related to two different defects, not to two charge states of one impurity. The changes from the red band in the bottom, to the yellow band in the middle, and to the green band on the top are due to the changes of the defect structures with growing layer thickness.

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