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Crystalline Structure Changes in GaN Films Grown at Different Temperatures

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Thin GaN films were grown on (0001) sapphire at various temperatures between 520 and 1050°C using metalorganic chemical vapor deposition (MOCVD). Optical properties and crystalline structures of the films were investigated by means of photoluminescence, Raman scattering, and X-ray diffraction. A noticeable structure transition occurred at around 750°C with higher growth temperatures favoring the hexagonal structure and lower ones the cubic. Defect formation was also seen to be temperature dependent. The yellow luminescence which was clearly observed in our 700–850°C films was attributable to the cubic and hexagonal structure mixing. The drastic reduction of yellow luminescence and the substantial enhancement of near band edge emission in the 950–1050°C films indicated that this temperature range is optimum for growing high quality wurtzite films.

KEYWORDS: GaN, crystalline structure, Raman scattering, photoluminescence

Recently, GaN and other wide gap semiconductors have attracted much attention because of the interest in fundamental physics and optoelectronic applications. Both metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) methods are widely used in growing GaN epitaxial films. Investigations of their electrical and optical properties which depend critically on influential factors such as substrate structure and orientation, epilayer thickness, buffer layer design, growth temperature, and V/III ratio were reported by numerous authors.[1–4] However, few reports addressed the optical property changes in a wide range of growth temperatures.[5,6] In this letter, we present experimental data for GaN films deposited at temperatures from 520 to 1050°C, investigated by means of photoluminescence (PL), Raman scattering, and X-ray diffraction. From the results, a phase transition from cubic to hexagonal structure was inferred to occur at around 750°C. The strong near band edge (NBE) emission, indicating a good quality wurtzite structure, was observed in our higher temperature (> 950°C) films. The yellow luminescence (YL) that appeared appreciably in our lower temperature (700–850°C) films, was believed to be due to the mixing characteristics of hexagonal and cubic structures.[7]

The GaN films deposited on (0001) sapphire were grown by MOCVD using NH_3 and trimethylgallium (TMGa) as the N and Ga precursors, respectively, where purified nitrogen rather than hydrogen was used as the carrier gas. To obtain good quality films, a thin GaN buffer layer was deposited at 520°C prior to the epilayer growth.[8] The top layers (~1–2 μm) were then prepared at temperatures between 520°C and 1050°C for the study. Characterizations of the GaN samples were carried out by PL, Raman, and X-ray measurements. For the PL experiments, we utilized a single monochromator (ARC Spectro PRO-500), a CCD detector (PI LN/CCD-576E), and a He-Cd laser (Kimmon IK5552R-F) operating at the 325 nm UV line for above the band gap excitation. The spectral accuracy of the PL data was better than 0.2 nm. The Raman setup consisted of a double monochromator (JY U1000), a multichannel photodiode array detector (PI IRY 1024G), and a mixed Ar^+/Kr^+ ion laser (Coherent Spectrum). The spectral resolution for Raman data was about 3 cm^{-1}. For X-ray studies, a five-circle double crystal diffractometer was employed in a grazing incidence geometry (≤0.1°) which enables us to detect the "in plane" off-axis lattice spacing.[9]

We present in Fig. 1 the room-temperature PL that showed distinct variations between 850 and 950°C. Below 950°C, the overwhelming YL around 560 nm (2.2 eV) is the sole dominant feature (intensities drawn in fractions of the higher temperature data), whereas the NBE at 365 nm (3.41 eV) is weak. The YL shifts from 565 to 610 nm as the temperature decreases from 850 to 700°C. However, from 950°C, the NBE is greatly enhanced in contrast to the YL reduction, which eventually becomes insignificant compared to that of the NBE

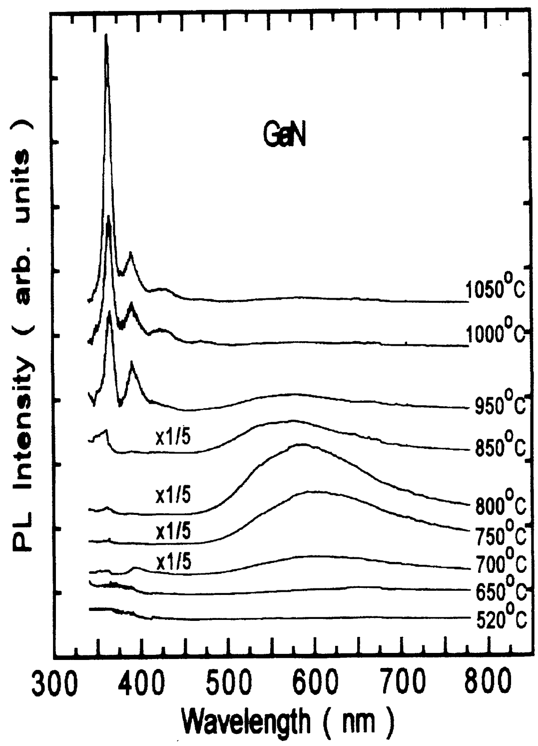

Fig. 1. Photoluminescence results of GaN films exhibiting the near band edge emission and yellow luminescence which are associated with the temperature-dependent structures.

(~1/800). The relative intensity changes in YL and NBE at about 950°C suggest that deep levels are overwhelmed by shallow ones because the YL is often related to either deep donors or deep acceptors.[10,11] The NBE band is known to contain significant exciton information in its low temperature (below 15 K) data.[12] Investigation of this and other optical properties is currently underway. The results will be published elsewhere.[13] Between 850 and 1050°C, the NBE is also accompanied by a side emission peak at 390 nm (3.19 eV) whose intensity is persistently smaller than that of NBE. Since the PL structures in the region of 3.0–3.3 eV were commonly assigned to donor-acceptor pair (DAP) recombinations by several groups,[10,11,14] we believe that this side peak is also attributable to DAP recombination. Besides, it is closely linked to the specific hexagonal phase found in our X-ray data (vide infra). Obviously, the defect formation is affected by both growth temperatures and structural changes.

Figure 2 shows the Raman spectra of our GaN films. Starting from 520°C, there is a lone broad high frequency band around 720 cm^{-1} opposite the small sapphire mode (417 cm^{-1}) on the left. At 650°C, a strong peak at 730 cm^{-1} emerges from the lone broad band and is accompanied by a satellite band at 768 cm^{-1}, which is probably a coupled plasmon-phonon mode.[15] Additionally, a new and broad low frequency band around 550 cm^{-1} also appears at this temperature. The two major peaks (730 and 550 cm^{-1}) are located close to the reported phonon frequencies in cubic GaN and are assigned to the LO and TO modes, respectively.[16] The spectra remain almost unchanged up to 700°C except that a minor structure starts to appear at 568 cm^{-1} on the shoulder

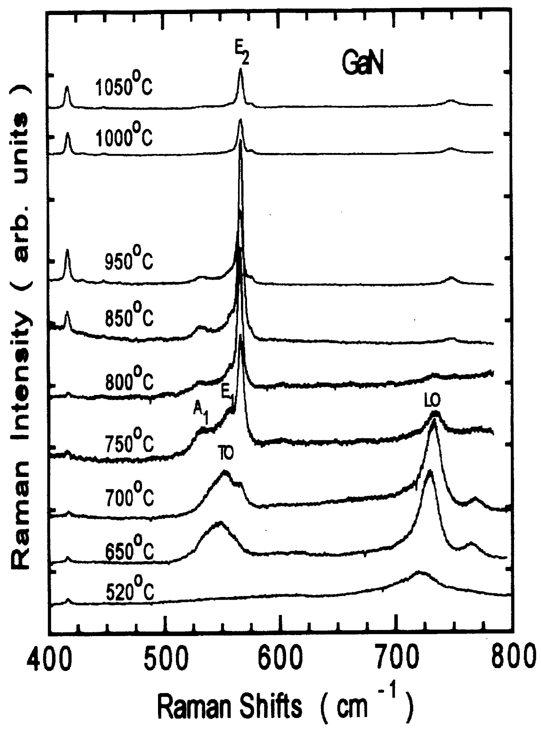

Fig. 2. Raman spectra of GaN films grown at temperatures from 520 to 1050°C. The transition occurring at around 750°C is attributed to the cubic to hexagonal structure change.

of the TO mode. This minor peak becomes the dominant structure for all temperatures higher than 950°C, which can be identified as the E_2 mode of the hexagonal GaN. At 750°C, the TO mode splits into the A_1(TO) and E_1(TO) modes, and the LO mode shows a significant drop in intensity. The concurrent appearance of the A_1, E_1, and E_2 modes indicates the predominance of the hexagonal structure at deposition temperatures higher than 750°C.[17] This argument is also supported by our X-ray measurements (vide infra). For the rest of the higher temperature data (from 800 to 1050°C), the overall spectral features appear similar to each other except for the variations of the E_2 mode intensity due to the film transparency increasing with temperature. Besides, the small structure at 577 cm^{-1} and the weak feature at 750 cm^{-1} resembling an up shifted LO mode are the sapphire signals. Their appearance is due to the same reason as that of the intensity drops of the E_2 mode. As far as the Raman line full width at half maximum (FWHM) is concerned, they occur from 25 to 35 cm^{-1} and from 15 to 20 cm^{-1}, respectively, for the TO and the LO modes of the films grown at temperatures between 520 and 700°C. These large widths indicate the polycrystalline zinc-blende characteristics in the lower temperature films. However, GaN films grown at temperatures higher than 750°C show much sharper linewidths, reflecting good epitaxial growth in wurtzite. Based on the preceding observations, we conclude that lower growth temperatures favor the higher symmetric cubic structure, and higher growth temperatures favor the lower symmetric hexagonal structure.

It is known that the (0002) planes of the hexagonal GaN have the same spacings and structure factors as the (111) planes of the cubic GaN.[18] Thus, it is difficult to determine these two structures using ordinary X-ray diffraction methods (θ-2θ scans and double crystal X-ray rocking curve). Since the two polymorphs have unique periodicities and stacking sequences, the intrinsic differences of the a-axis lattice constants can be distinguished with the "off-axis" diffraction peaks from inclined planes.[19] Hence, grazing incidence X-ray diffraction (GIXD) was performed on the GaN films grown at 650–1050°C. As shown in Fig. 3, the GIXD results exhibit very significant features. For the 650°C sample, the diffraction peak at 20° is from the (200) planes of the zinc-blende GaN. For the 950–1050°C samples, the peak at 16.2° almost coincides with the theoretical angle for the ($10\bar{1}0$) planes of the wurtzite GaN. Good alignment of the c-axis normal to the substrate plane not only promotes the intensity of the 16.2° peak but also accounts for the appearance of DAP and NBE enhancement in PL data. By rotating the 1000°C sample about its surface normal direction (ϕ-scan), the GIXD diffraction peaks can be observed to recur every 60° (see the inset), which unambiguously reveals the hexagonal characteristic of the film. The 750 and 800°C data are alike showing two strong peaks except for an inferior X-ray diffraction appearance. The sharp one at 19.2° is from the hexagonal ($10\bar{1}1$) planes and the broad one centered around 17.6° the unresolved cubic (111) and hexagonal (0002) planes. This structure demonstrates unusual

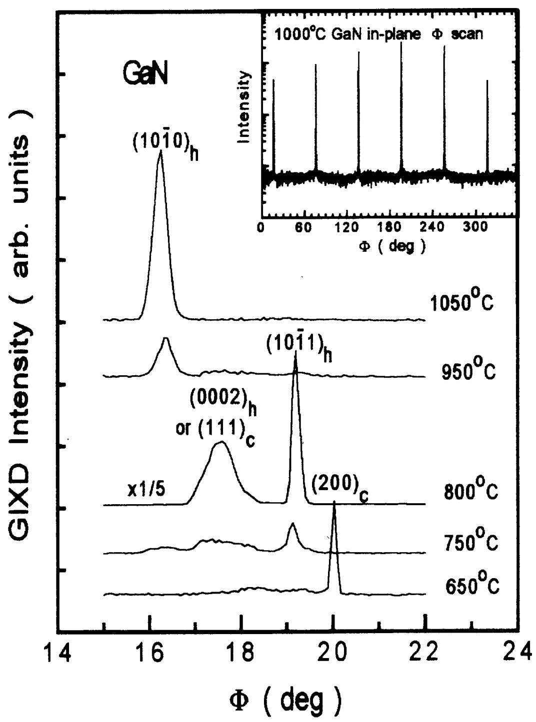

Fig. 3. Grazing incidence X-ray diffraction results of GaN films revealing the hexagonal and cubic structures formed preferably at higher and lower temperatures, respectively. The inset shows the six-fold symmetry in the 1000°C sample by an in-plane ϕ scan.

linewidth and position shifts from the perfect zinc-blende and wurtzite structures (17.2° and 17.3°). We believe this is due to the compounded effects of intrinsic strain and crystalline structure mixing. Therefore, the onset of crystalline structure change is inferred to occur at around 750°C. This is consistent with the conclusion we draw from the Raman and PL results.

In summary, we have made systematic measurements on GaN films deposited at different temperatures. Deep levels responsible for yellow luminescence appeared favorably in the mixed structure grown between 700 and 850°C. Near band edge luminescence was greatly enhanced between 950 and 1050°C, indicating that high quality samples can be attained through careful temperature control. Based on the consistency of our PL, Raman, and GIXD results, a transition associated with the cubic to hexagonal structure change around 750°C can be assigned.

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