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Indium assisted hydride vapor phase epitaxy of GaN film

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In order to increase the migration length of adatoms in hydride vapor phase epitaxy (HVPE) of GaN films, indium was used as a surfactant in HVPE growth. For samples with indium, an increase of crystalline quality was confirmed by X-ray diffraction measurements, and an improvement of surface morphology was also observed. SIMS analysis showed that indium was incorporated in the as-grown GaN film, and indium related photoluminescence (PL) was also detected.

Key words: GaN, substrate, HVPE, surfactant, SIMS.

Introduction

The large lattice and thermal mismatches between GaN and the most commonly used sapphire/SiC substrates have required the development of a native GaN substrate. HVPE is a promising technique for growing thick GaN films for substrate applications [1-3]. The growth rate is very high in the HVPE process compared with other epitaxial techniques. In most cases, the growth rate can vary in the range 20-300 μm/h. A critical point in a high growth rate epitaxial process is the enhancement of the surface mobility of adsorbed species. Recent work has demonstrated that indium can serve as an efficient surfactant for the growth of GaN by molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD) [4-8]. An interesting question is to know whether it can play the same role in HVPE growth. The effect of indium on the structural and optical properties of thick HVPE GaN films is now reported.

Experimental Growth and Measurements

The GaN films were grown in a horizontal HVPE reactor at atmospheric pressure. The GaCl formed upstream inside the reactor by reaction of the liquid gallium with HCl at 850 °C. Nitrogen was used as a carrier gas, and NH_3 and GaCl mixed on the top surface of the substrate in the showerhead structure reactor. In order to study the influence of indium on the growth process, an indium boat was also introduced in the upstream of the reactor; it reacted with HCl at about 600 °C to form InCl. The geometric and spatial parameters of the indium boat were optimized during the growth. The thicknesses of the as-grown GaN films were about 12 μm. The samples grown with and without indium were called In-doped and undoped GaN, respectively.

X-ray diffraction (XRD) measurements were performed with a Philips MRD system, and the analysis by Secondary Ion Mass Spectrometry (SIMS) was performed with a Cameca IMS-6F instrument. The surface morphology was observed in a JEOL scanning electron microscope (SEM) at 20 keV. Ultraviolet photoluminescence (PL) spectra were measured with the 325 nm line from a He-Cd laser with an excitation power of 4 mW. The samples were installed on the cold finger of a helium cycling cryostat, in which the temperature could be changed from 10 K to room temperature.

Results and Discussion

XRD spectra showed that the HVPE GaN films exhibited the common epitaxial relationship: $(0002)_{GaN}//(0001)_{sapphire}$, $[11\bar{2}0]_{GaN}//[10\bar{1}0]_{sapphire}$. The full width at half maximum (FWHM) values of 002 and 102 GaN peaks were determined (Table 1). The improvement of the crystalline quality for the In-doped samples was shown by comparing the measured FWHM data. Both the symmetric and asymmetric FWHM were smaller for the In-doped sample. A reduction of point defects as well as an improvement of crystalline quality has

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Table 1. FWHM of XRD results of both undoped and In-doped GaN films

XRD results (unit: arcsec)	(002) scan	(102) scan
Undoped	464	534
In-doped	383	441

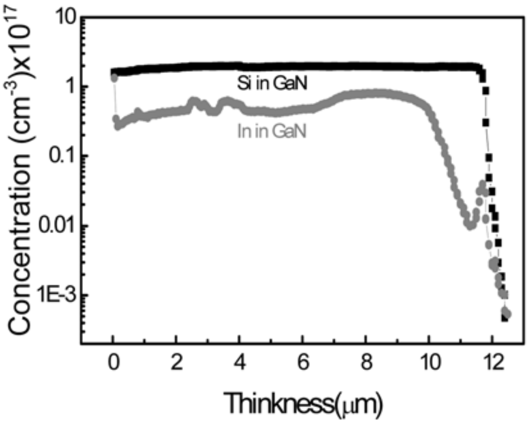

Fig. 1. Profile of concentration of Si and In in an In-doped GaN film.

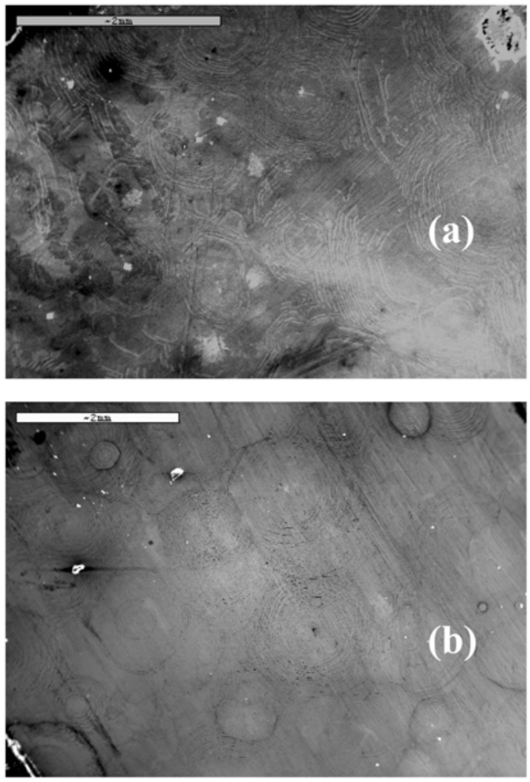

Fig. 2. Surface morphologies observed by SEM of (a) undoped and (b) In-doped GaN films grown by HVPE.

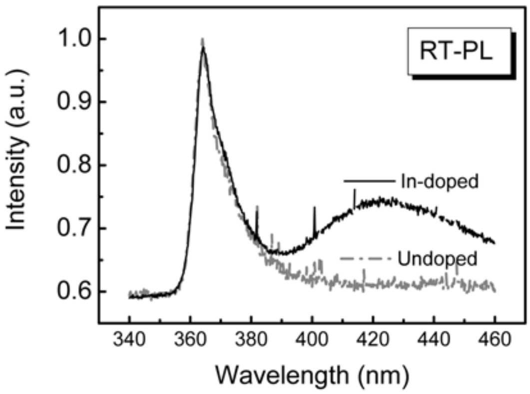

Fig. 3. RT PL of undoped and In-doped GaN films.

been demonstrated in MOCVD [4, 7] and MBE grown GaN films [8].The values from the XRD data are closely related with the dislocation density inside the GaN films. The reduction of the FWHM indicates that both the edge type and screw type dislocation densities were reduced for the In-doped GaN.

SIMS measurements were performed in order to check the residual indium concentration inside the In-doped HVPE GaN films. Silicon was chosen as a reference to quantify the indium concentration. The Si concentration was previously determined by room temperature Hall measurements assuming that all Si atoms inside the films were ionized at the measurement temperature. As shown in Fig. 1, an indium concentration of about 5.10^{16} at/cm^3 was found. This result is different from those obtained by MOCVD and MBE. Although the process takes place at a much lower temperature (several hundreds degree centigrade), some indium atoms are easily trapped before being evaporated due to the high growth rate in the HVPE process.

The surface morphologies of undoped and In-doped samples were observed by SEM (Fig. 2(a, b)). It is obvious that the grain size in (a) is smaller than in (b), and there are much more grain boundaries on the surface of (a). Optical observations at a larger scale (not shown here) also shows that the sample grown with indium is smoother. This is consistent with the results observed in MOCVD and MBE grown GaN films.

The role of indium on the optical properties has also been studied. Room temperature (RT) PL spectra of both undoped and In-doped samples are shown in Fig. 3. The solid lines correspond to the PL spectra of undoped samples, whereas the PL from the In-doped GaN is shown by the dashed line. The band gap energies of the peaks seem the same in both samples. It was found that a broad blue band peak appears in the In-doped sample but not for the undoped sample. Considering the different growth processes between the two samples, the formation of the blue band should be indium-doping related.

PL spectra of In-doped samples at different temperatures were also measured as shown in Fig. 4. Two main peaks remain in the spectra from 10 K to RT, whereas the relative intensity varies with the temperature. At 10 K, the blue band is much stronger than the band gap emission around 357 nm, and some small

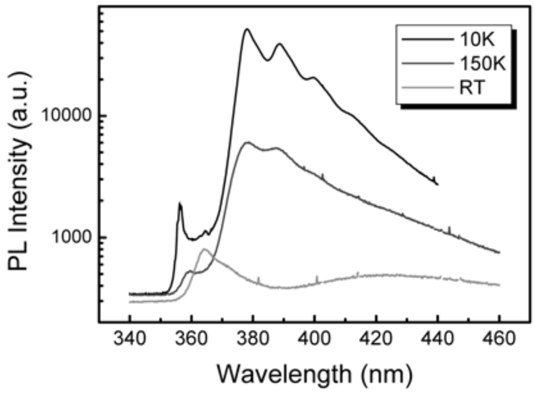

Fig. 4. The temperature-dependent PL spectra of the In-doped GaN film.

peaks due to interference can be seen on the shoulder of the blue band. The band gap emission shrinks and broadens very quickly when the temperature is increased to 150 K, but the blue band remains strong. As the temperature is increased much higher, the blue band is quenched rapidly, at the same time the band gap emission dominates the spectrum, and the peak intensity becomes strong again. According to these results, there should be an electron transfer process inside the sample in the low temperature region, and a study on the detailed mechanism is still under way.

The growth mechanisms are different between MOCVD and HVPE although both of them involve vapor phase epitaxy, but the results shown above indicate that the role of indium is similar, it acts as a surfactant in both the two processes.

Conclusions

HVPE growth of GaN with and without indium has been performed. For samples with indium as a surfactant, the crystalline quality and surface morphology have been improved. The incorporation of indium in the as-grown GaN film was verified by SIMS measurements, and strongly influences the optical properties of In-doped GaN films. Indium-assisted growth is confirmed to be an alternative method for HVPE growth of GaN films.

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