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Properties of GaN grown on sapphire substrates

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Epitaxial growth of GaN on sapphire substrates using an open-tube growth furnace has been carried out to study the effects of substrate orientation and transfer gas upon the properties of the layers. It has been found that for the (0 0 0 1) substrates, surface appearance was virtually independent of carrier gas and of doping levels. For the $(1\bar{1}02)$ substrates surface faceting was greatly reduced when He was used as a transfer gas as opposed to H_2. Faceting was also reduced when the GaN was doped with Zn and the best surfaces for the $(1\bar{1}02)$ substrates were obtained in a Zn-doped run using He as the transfer gas. The best sample in terms of electrical properties for the $(1\bar{1}02)$ substrate had a mobility greater than $400\,cm^2\,V^{-1}\,sec^{-1}$ and a carrier concentration of about $2 \times 10^{17}\,cm^{-3}$. This sample was undoped and used He as the transfer gas. The best (0 0 0 1) sample was also grown undoped with He as the transfer gas and had a mobility of $300\,cm^2\,V^{-1}\,sec^{-1}$ and a carrier concentration of $1 \times 10^{18}\,cm^{-3}$.

1. Introduction

Gallium nitride is a III–V semiconductor compound having a direct bandgap equal to ~3.4 eV. This large bandgap energy makes gallium nitride potentially important as a light emitter in the spectral range from the visible to the near ultraviolet. In addition, the chemical and thermal stability of the compound offers promise in the area of high temperature electrical device applications. Previous studies [1–6] have shown that gallium nitride can be grown as n-type epitaxial layers on sapphire substrates. Pankove [1] and the others [4, 6] have produced intrinsic layers with zinc doping. These researchers then grew n-layers covered by intrinsic layers (i–n structure) on which metal contacts could be placed (m–i–n structure). Biasing the m–i–n structure with the appropriate voltage gave electroluminescence that varied in wavelength from the near ultra-violet to orange depending upon bias polarity and magnitude and the growth conditions for the crystal [1]. Recent studies have lead to GaN LEDs with applied voltage requirements as low as 3.2 V for blue and 2.4 V for orange [4].

This study was initiated to investigate the possible difference in growth on (0 0 0 1) sapphire and $(1\bar{1}02)$ sapphire in order to reconcile differences in the results of Pankove [1] and Ilegems [2, 3]. No other orientations were considered at the time. The investigation also included looking at the effects of carrier gas on the quality of the epitaxial layers. The effects of these two parameters on electrical and optical properties of GaN and on the surface morphology of the GaN layers were studied. The results obtained are reported and compared to recently reported results by other investigators.

2. Experimental procedures

The experimental runs were designed to investigate the effects of substrate orientation and transfer gas upon the properties of the epitaxial GaN layers. An open-tube growth furnace (Fig. 1), similar to that of Maruska and Tietjen [5], having three temperature zones, was used. A typical run had a temperature of 925° C in the gallium zone. Anhydrous hydrogen chloride, HCl, produced a

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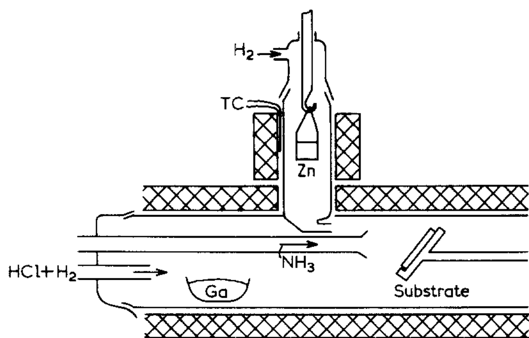
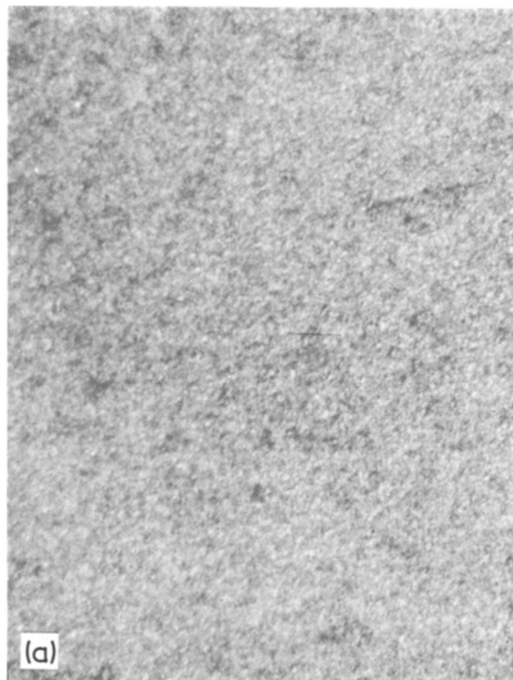
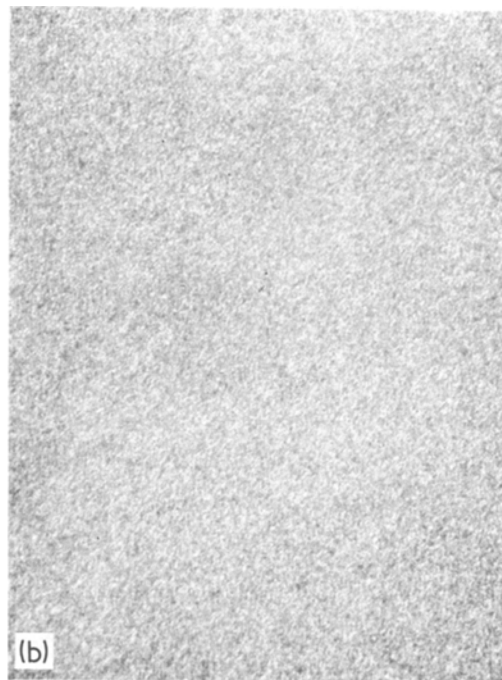


Figure 1 Schematic diagram of furnace for growing GaN.

sub-chloride molecule of gallium that was transported by hydrogen or helium carrier gas. The nitrogen source, NH_3, exited from a flow tube about $\frac{1}{2}$ in. from the sapphire substrate which was at 950° C. Sapphire substrates with an optical quality polish were subjected to a 5 min heat soak at the run temperature prior to turning on the HCl. Growth times were normally 5 min with a growth rate of about $100\,\mu m\,h^{-1}$. Some samples were doped with zinc to study the effect on the GaN properties. The zinc temperature was variable and was usually between 425 and 475° C with a flow of the chosen transfer gas carrying the zinc atoms to the substrate.





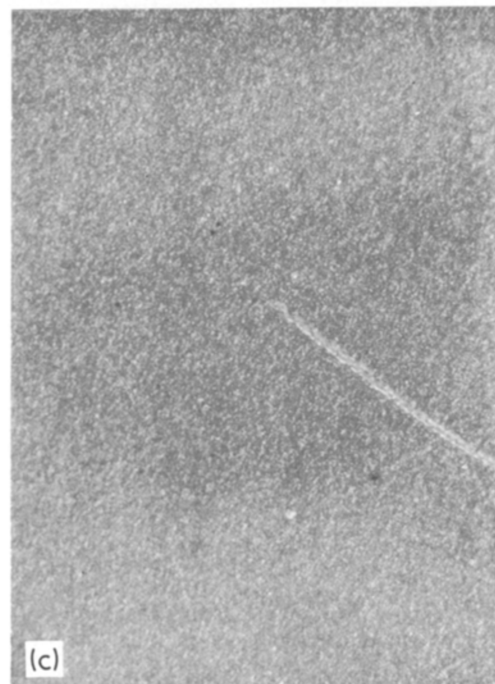


Figure 2 Growth on (0001) substrates (510 ×); (a) undoped, H_2 transfer gas, (b) Zn-doped, H_2 transfer gas, (c) Zn-doped, He transfer gas.

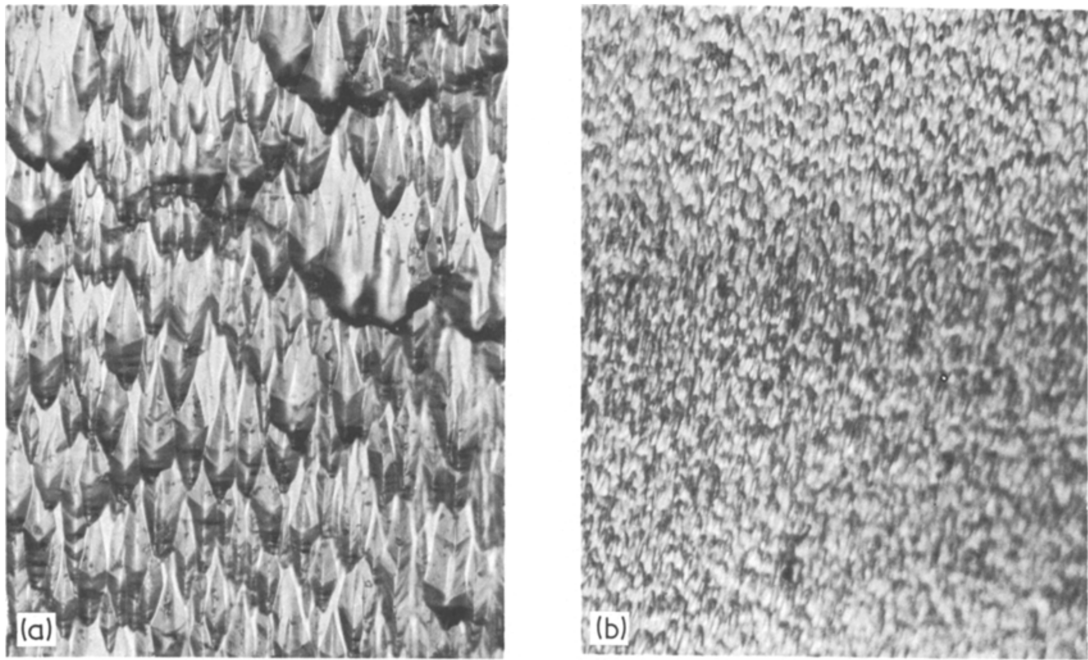


Figure 3 Growth on $(1\bar{1}02)$ substrates; (a) undoped, H_2 transfer gas (510 ×), (b) undoped, He transport gas (340 ×).

Electrical properties were determined from resistivity and Hall effect measurements on bridge samples. The bridge sample was shaped by sandblasting away the excess GaN through a mask. A magnetic field of 4000 Gauss and longitudinal current of 20 mA were used. X-ray data were obtained using a Laue back-reflection camera and an X-ray diffractometer. Surface features were studied with Normarski optical microscopy. Photoluminescence spectra were obtained by exciting the GaN with an RCA He–Cd laser generating several milliwatts at 3250 A. The GaN emission (at liquid nitrogen and room temperature) was analysed by a spectrometer equipped with a quality prism and a photomultiplier (RCA31025). The radiation was chopped and the detected signal processed by a lock-in amplifier and recorded as a photoluminescence spectrum on an x–y recorder, the x-input of which was controlled by the wavelength drive of the spectrometer.

3. Results

GaN films grown on sapphire substrates have a surface texture that is strongly dependent on the crystallographic orientation of the substrates. The doped and undoped layers grown on the (0001) substrates are relatively smooth (Fig. 2) whereas the layers grown on the $(1\bar{1}02)$ substrates with H_2 as the transfer gas appear to be composed of nucleated islands which have coalesced during growth and the surface shows a strongly faceted structure (Fig. 3). The Laue pattern and X-ray diffraction data indicate that the layers are, nevertheless, single crystalline. The films on the (0001) sapphire substrates have a (0001) orientation (Fig. 4). The layers on the $(1\bar{1}02)$ substrates were oriented in the $(1\bar{1}20)$ direction which has the two-fold symmetry seen in Fig. 5.

When the transfer gas is inert, i.e., He, the degree of faceting on the $(1\bar{1}20)$ GaN surface is greatly reduced and the nucleated islands are much smaller (Fig. 3b). The carrier gas used for the (0001) growths had no apparent effect on the surface (Fig. 2). Similarly, when zinc was added to the wafer, the surface appearance was not noticeably changed. For the $(11\bar{2}0)$ GaN samples, however, the surface faceting decreased greatly, when zinc was added (Fig. 6). The best surface aspect for the $(11\bar{2}0)$ orientation was obtained with an inert carrier gas and zinc doping (Fig. 6). Jacob *et al.* [4] noted the better surface aspect in their zinc-doped samples but offered no explanation. While the results for the $(11\bar{2}0)$ layers reported here generally agree with those

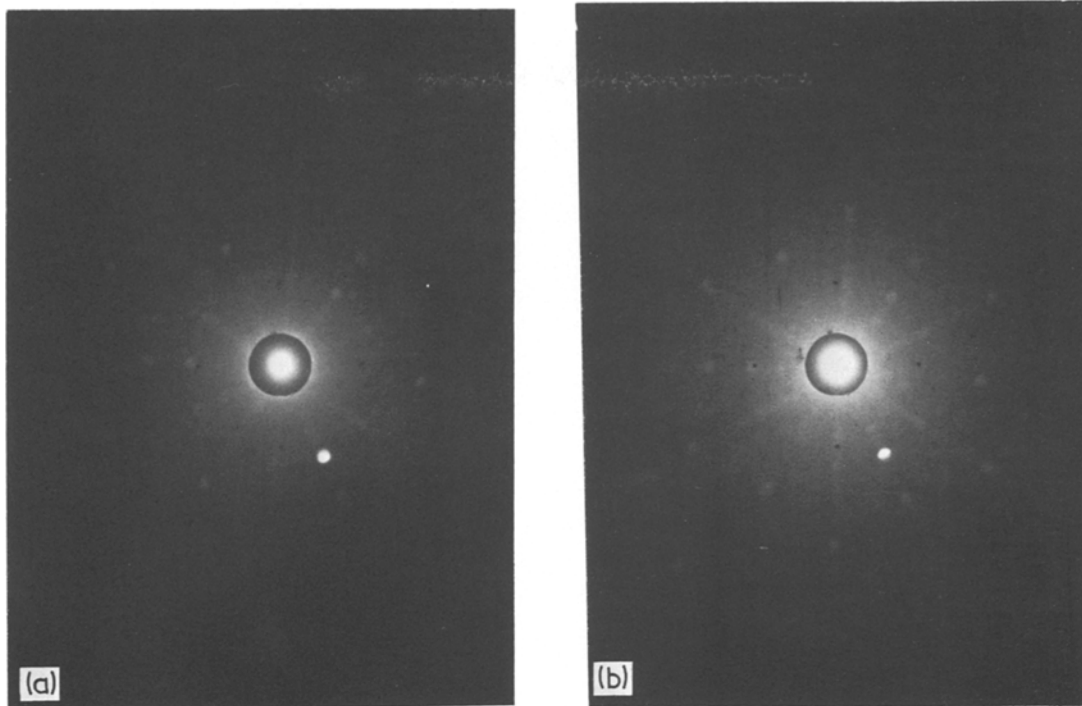


Figure 4 Laue photograph of growth on (0 0 0 1) substrate; (a) sapphire substrate (0 0 0 1), (b) GaN layer (0 0 0 1).

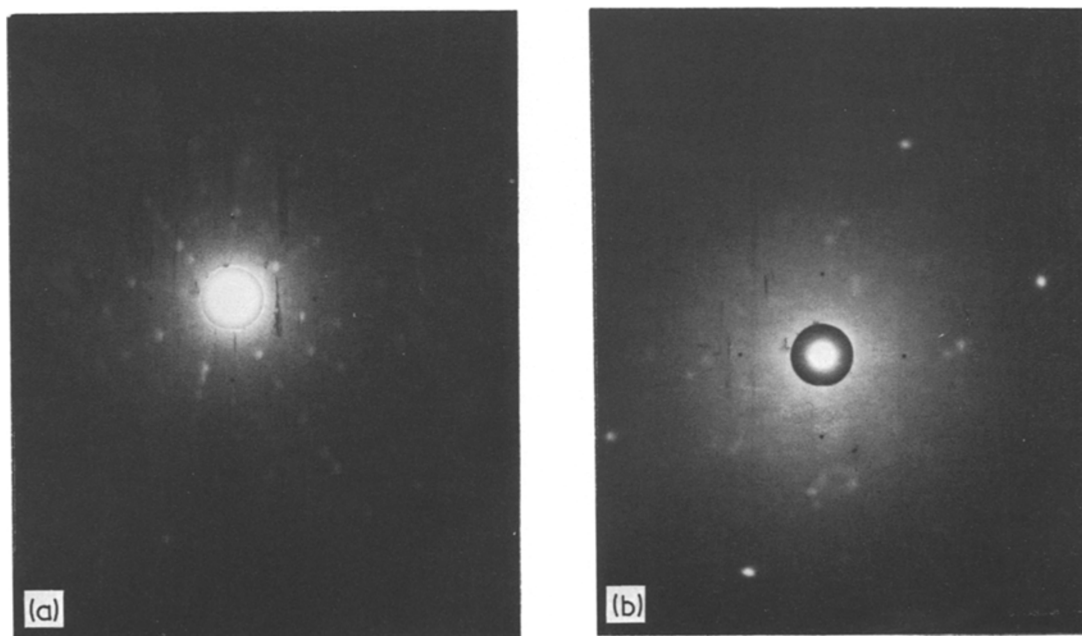
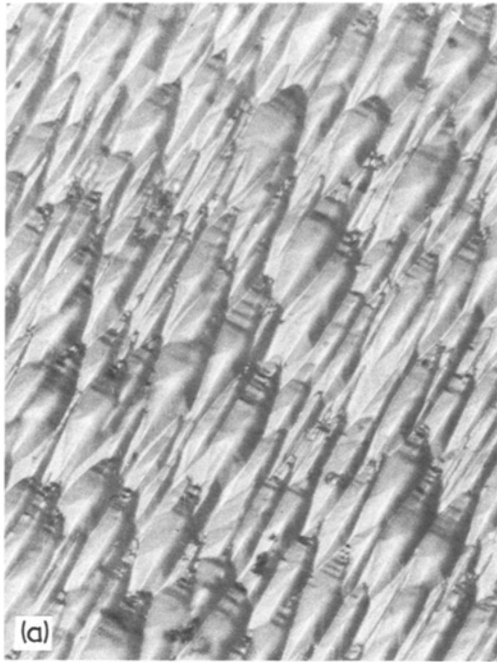
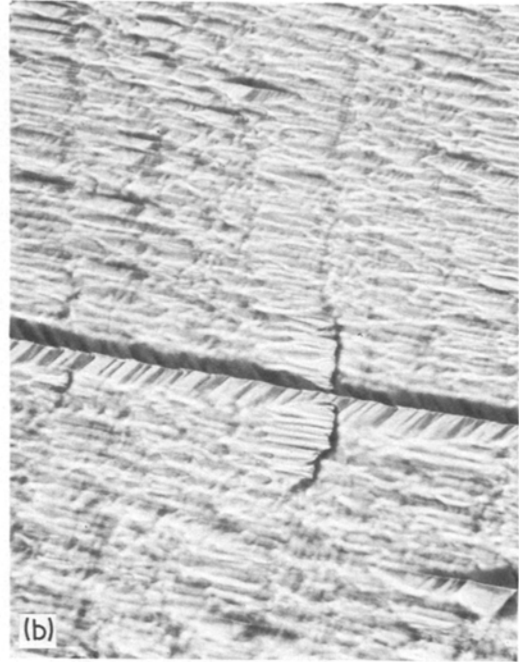


Figure 5 Laue photograph of growth on $(1\,\bar{1}\,0\,2)$ substrate; (a) sapphire substrate $(1\,\bar{1}\,0\,2)$, (b) GaN layer $(1\,1\,\bar{2}\,0)$.





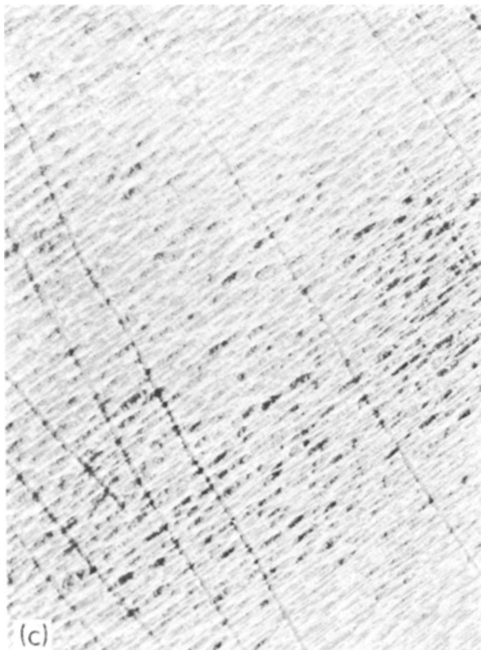


Figure 6 Effects of zinc doping on surface aspect of $(1\bar{1}20)$ samples. (a) Undoped, H_2 transport gas; (b) Zn-doped, H_2 transport gas; (c) Zn-doped, He transport gas (all 510 ×).

of Jacob *et al.*, the (0001) layers reported here were much smoother than their (0001) layers and showed no dependency on carrier gas or doping.

The electrical properties of the GaN were determined from Hall effect and resistivity measurements made on bridge-shaped samples. For undoped n-layers with a hydrogen carrier gas, the concentration of carriers was typically about 1 to 2×10^{19} carriers cm^{-3}, regardless of substrate orientation. It was found that the samples grown on (0001) substrates had Hall mobilities that were typically about $100 \, cm^2 V^{-1} sec^{-1}$; whereas, the samples grown on $(1\bar{1}02)$ substrates had mobilities around $80 \, cm^2 V^{-1} sec^{-1}$. For undoped samples using He as the carrier gas, the best sample in terms of electrical properties had a carrier concentration of 2×10^{17} carriers cm^{-3} and a mobility of greater than $400 \, cm^2 V^{-1} sec^{-1}$ and was grown on a $(1\bar{1}02)$ substrate. The best (0001) had a carrier concentration of 1×10^{18} carrier cm^{-3} and a mobility of 300 $cm^2 V^{-1} sec^{-1}$.

By varying the temperature of the zinc source between 400° C and 475° C, the resistivity of the resultant layer varied from about 0.005 Ω cm to semi-insulating. Table I lists the results from a series of runs using a H_2 carrier gas and various Zn temperatures.

The photoluminescence (PL) spectra of the undoped samples normally showed a peak at 3.44 eV for liquid nitrogen temperatures regardless of substrate orientation (Fig. 7). This peak

TABLE I Effects of Zn doping on electrical properties of (0 0 0 1) GaN

Zn temperature (° C)	Resistivity (Ω cm)	Mobility ($cm^2 V^{-1} sec^{-1}$)	Carrier concentration (no. cm^{-3})
<400	0.006	96	1.2×10^{19}
425	0.03	79	2.7×10^{18}
450	0.3	15	1.5×10^{18}
470	semi-insulating	-	-

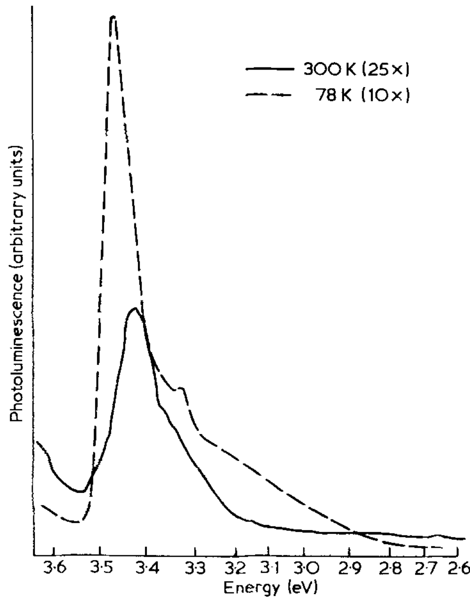


Figure 7 Photoluminescence spectra of undoped GaN.

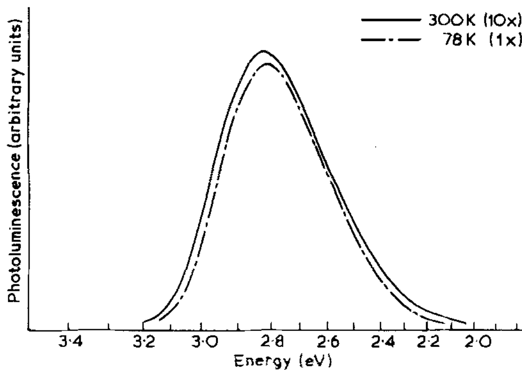


Figure 8 Photoluminescence spectra of Zn-doped GaN.

shifts to 3.40 eV at room temperature and is about an order of magnitude lower in intensity. When the GaN layers are heavily doped with zinc, the photoluminescence shifts to a broad band at about 2.8 eV (Fig. 8). While the location of the peak has very little temperature dependence, the intensity of photoluminescence is greatly enhanced at 78 K over 300 K. The photoluminescence was not affected by substrate orientation.

Photoluminescence data indicated two interesting aspects. There appears to be a zinc contamination problem in the glass tube after a zinc run has been made. It was found that unless the tube was removed and cleaned the 2.8 eV line could be observed in an apparently undoped (0 0 0 1) sample as many as four runs after a zinc doping run had been made. Secondly, the photoluminescence spectra of a $(1\bar{1}02)$ sample would not show this 2.8 eV line under similar circumstances implying that zinc is more readily incorporated into the (0 0 0 1) layer. This differential doping tendency is in agreement with the results of Shintani and Minagawa [6] and the contamination problem could explain the lack of control they had for runs in which they attempted light zinc doping.

4. Concluding remarks

In summary, GaN epitaxial layers have been grown using different carrier gases on sapphire substrates with different orientations. The photoluminescence spectra showed no substrate effects. Using hydrogen as the carrier gas, the carrier concentration was virtually independent of substrate orientation, while the Hall mobility of the $(1\bar{1}02)$ substrate was about 20% lower than for the (0 0 0 1) substrate samples. However, for the He carrier gas, the best sample in terms of carrier concentration (2×10^{17}) and mobility ($400 cm^2 V^{-1} sec^{-1}$) was grown on a $(1\bar{1}02)$ substrate.

The surface features for the (0 0 0 1) layers are very smooth and show no distinguishable dependency on carrier gas. The $(11\bar{2}0)$ layers grown on $(1\bar{1}02)$ substrates are highly faceted when grown undoped in a hydrogen carrier gas. The faceting is greatly reduced when helium is used as a carrier gas and/or when zinc is added to the material. Also, for either substrate, the carrier concentration was lower when helium carrier gas was used than when the hydrogen carrier gas was employed.

The photoluminescent peak for zinc-doped samples was very broad and was centred about

2.8 eV and showed no energy shift between room temperature and liquid nitrogen temperature. This is in agreement with previous work by Pankove [1], Ilegems [2, 3], and Grimmeiss [8], but different from more recent results by Shintani and Minagawa [5].

The photoluminescent peaks of the undoped layers, 3.44 eV at liquid N_2 temperature, were in general agreement with the results of Jacob *et al.*, [4] and Matsumoto and Aoki [6] with the slight variations between samples being reasonably explained by variations in stress of the samples as reported by Matsumoto and Aoki.

The large difference in surface aspect between the (0 0 0 1) and the $(1\bar{1}02)$ substrates is not understood and has not been reported previously. Most literature indicates that growth on the (0 0 0 1) substrate also had a significant amount of the faceting. In fact, the faceting may be essential in the production of LED's according to the theory of Maruska and Stevenson [9]. Clearly, more investigation into the effects of transfer gas and crystal orientation on surface morphology is needed to explain the growth characteristics of gallium nitride layers on sapphire substrates.

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