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# High Quality GaN Grown by Reactive Sputtering

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## ABSTRACT

Gallium nitride films were grown by reactive rf magnetron sputtering on sapphire substrates. Crystalline $(11\overline{2}0)$ GaN films were obtained on $(01\overline{1}2)$ sapphire at substrate temperatures between 640-680 °C. High $N_2$ partial pressures are required to crystalize the GaN films. Nitrogen incorporation and crystal quality of GaN films are examined as a function of substrate temperature and nitrogen partial pressure. Band gaps of 3.4 eV, and photoluminescence peaks as narrow as 11 meV are reported for sputtered GaN films.

Gallium Nitride ($GaN_x$) is a direct III-V wide-gap semiconductor having potential applications for stimulated emission in the blue, violet, and ultraviolet spectral range. Compared to II-VI materials such as ZnSe, GaN is strongly bonded and thus more resistant to radiation damage and electromigration. Two principal barriers exist for the development of practical GaN optical devices: the difficulty of producing p-type conducting material, and the lack of a convenient substrate for epitaxial growth.

GaN is most often grown by chemical vapor deposition (CVD) techniques and on basal plane sapphire substrates. Using CVD and AlN buffer layers the highest mobilities (350 $cm^2/Vs$) and lowest carrier concentrations ($1x10^{17}$ $cm^{-3}$) for GaN films have been obtained[1]. Other deposition methods include reactive molecular beam epitaxy[2,3], reactive sputtering[4,5,6] and solution growth[7]. Amano[8] demonstrated p-type conduction using low-energy electron-beam irradiation on Mg-doped GaN. The mechanism responsible for converting n-type GaN to p-type by this procedure is not completely understood.

In this paper we investigate the effect of various deposition parameters on the structure, composition, and optical properties of GaN to determine the difficulties in producing stoichiometric material. Reactive magnetron sputtering was used for this purpose because it conveniently produces material with optical properties comparable to CVD and MBE. The films were characterized by x-ray diffraction

(XRD), Rutherford back scattering (RBS), optical absorption, and photoluminescence.

The GaN films were deposited by reactive rf magnetron sputtering using an US-Gun-II 2-inch modular source. The target was pure gallium (99.999999%) held in a stainless steel cup. Gallium melts slightly above room temperature (29.8 °C), so the target, although water cooled, was liquified by electron bombardment heating. Sapphire substrates, cut $(01\overline{1}2)$, were attached to an electrically isolated heater block held 6.5 cm above the target. We have also used (111) GaAs substrates to grow basal plane GaN. Substrate temperature was varied from 450-700 °C.

Before deposition, the chamber was evacuated to less than $10^{-6}$ Torr, and then backfilled with a mixture of argon and nitrogen gas to 5-30 mTorr. The nitrogen flow was varied from 0-100% while the total flow of $N_2$ and Ar was maintained at 100 sccm. The target was presputtered for 1 hour; first in 100% argon to remove surface impurities, and then in a 70 $N_2$:30 Ar mixture to create a nitrided surface on the gallium target. The growth rate on the substrate was measured by a quartz-crystal oscillator calibrated with a stylus profilometer. Typical film thicknesses were 1-2 μm. After deposition the substrates were cooled in 100% $N_2$ to 200 °C. The growth rate of the $GaN_x$ films is shown in Figure 1 as a function of nitrogen partial pressure.

Films deposited over a range of temperature, pressure, and $N_2$ flow rate were examined by RBS and XRD. High $N_2$

partial pressure was necessary to form a crystallize GaN phase. Continuing to raise the total pressure, however, eventually caused the nitrogen concentration and the x-ray peak intensities to diminish. This may be related to the slower deposition rate at high pressures allowing increased nitrogen desorption. A total pressure of 10 mTorr was found to give both reasonable deposition rate and nitrogen incorporation. Below 60% nitrogen in the atmosphere, N/Ga ratios were less than .80 and no x-ray peaks were observed. For 60%-95% $N_2$, good crystallinity, consistent composition (N/Ga~0.85), and steady growth rates were obtained. Nitrogen atmospheres over 95% resulted in amorphous films, probably due to the lower sputtering efficiency of $N_2$ compared to Ar.

Using the conditions of 70% $N_2$ and 10 mTorr total pressure the substrate temperature was varied. Crystallinity was observed by x-ray diffraction at temperatures above 580 °C as shown in Figure 2. Between 580 and 625 °C relatively weak (0002) and $(11\overline{2}0)$ GaN peaks emerge. Above 625 °C the $(11\overline{2}0)$ intensity increases rapidly until, in the range between 640-680 °C, all peaks vanish except for a strong $(11\overline{2}0)$ signal. This preferential orientation of $(11\overline{2}0)$ GaN on $(01\overline{1}2)$ sapphire substrates was also predicted and observed by Sasaki and Zembutsu[9]. The width of the x-ray peak for the 660 °C film in Figure 2c is 25 minutes. For temperatures above 700 °C, the diffraction pattern again becomes featureless, indicating a transition to an amorphous film. The principal peak intensities are plotted in Figure 3a as a function of temperature.

RBS indicates that initially nitrogen content rises as the temperature is increased. The maximum N/Ga ratio is .92 at 625 °C and decreases slightly as the temperature increases to 680 °C. As shown in Figure 3a and 3b, nitrogen content and x-ray intensities decrease rapidly for substrate temperatures over 700 °C. Higher temperatures should result in larger numbers of nitrogen vacancies. It appears sufficient surface temperature is required for the formation of GaN, however, excessive temperatures cause large amounts of nitrogen to leave the film. We have found this effect can be somewhat reduced by cooling the substrates after deposition in a high partial pressure of nitrogen. At 680 °C, films cooled in 20 mTorr $N_2$ displayed N/Ga ratios of 0.83, while films cooled under vacuum were 0.57.

Since nitrogen vacancies act as shallow donors, higher N/Ga ratios should correspond to larger resistivities. Resistivity was measured with a four-point probe, and followed the nitrogen incorporation as expected. Spectral transmittance was measured over a wavelength range of 280 to 700 nm. The Tauc plot in Fig 4a shows that Eg = 3.4 eV for a film grown at 660 °C. This corresponds to the bulk GaN value at room temperature. Photoluminescence (PL) was measured at room temperature using a HeCd laser (325 nm), and confirms the band gap to be 3.4 eV. The full width half maximum of the photoluminescence peak is 11 meV. This is the narrowest room temperature peak observed for GaN films grown by any deposition technique.

In summary, we have defined a narrow range of temperature for crystalline growth of GaN on $(01\bar{1}2)$ sapphire by rf sputter deposition. High nitrogen partial pressures are required to crystallize GaN films. However surprisingly, higher pressures decrease nitrogen incorporation, possibly due to the reduction in deposition rate allowing increased desorption of nitrogen. Substrate temperatures above 700°C, at 10 mTorr pressure, also lower N/Ga ratios. Without sufficient incorporation of nitrogen to form the GaN phase, the films are amorphous perhaps due to the low melting temperature of the Ga:N solid solution. Nitrogen vacancy formation remains a problem in GaN. Growth methods need to be devised to increase the sticking probability of nitrogen atoms at the film surface. Reducing the crystallization temperature by using more reactive gases or ion-assisted processes are possible approaches.

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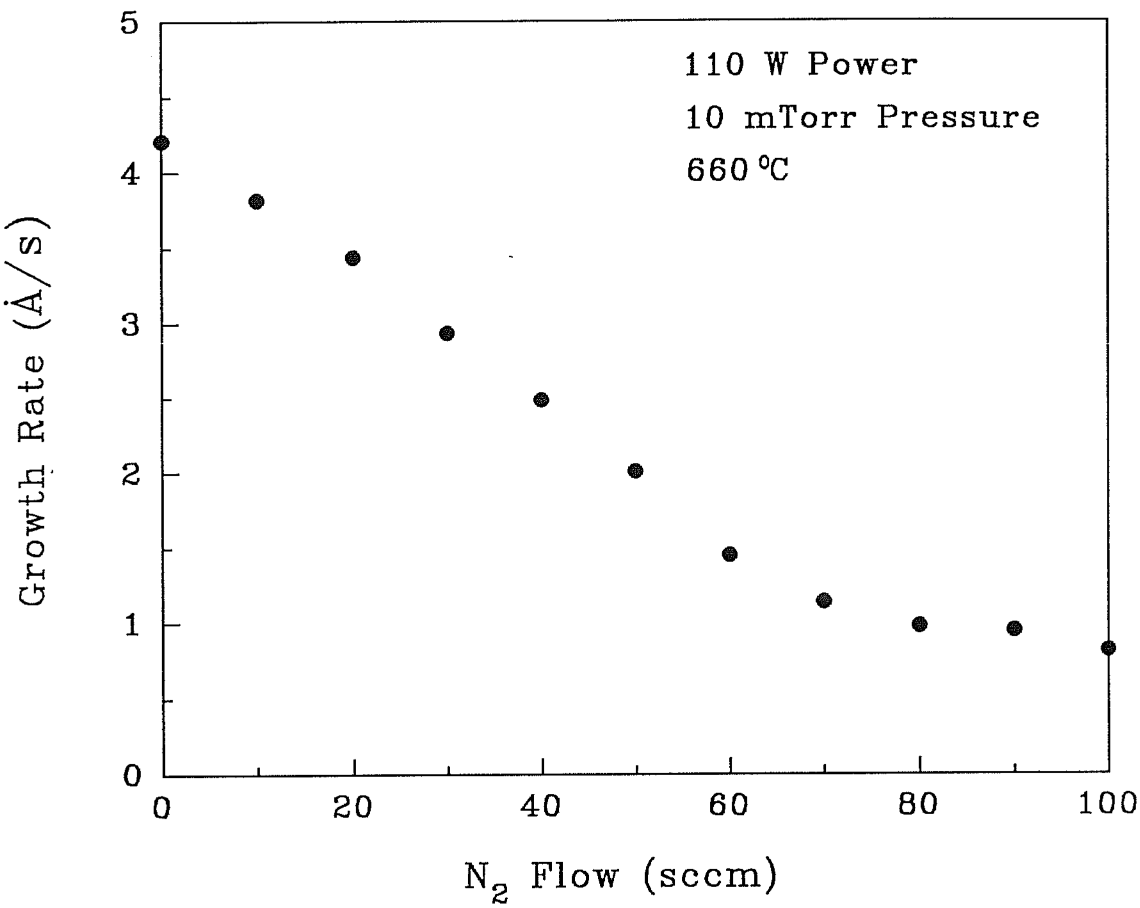
**Figure Captions**

Figure 1. Growth rate of GaN films as a function of nitrogen flow rate. Combined flow rate of $N_2$ and Ar is maintained at 100 sccm and total pressure 10 mTorr.

Figure 2. (a) X-ray diffraction pattern of GaN grown at 70% $N_2$, 10 mTorr pressure, 500 °C; (b) 580 °C; (c) 660 °C; and (d) 700 °C.

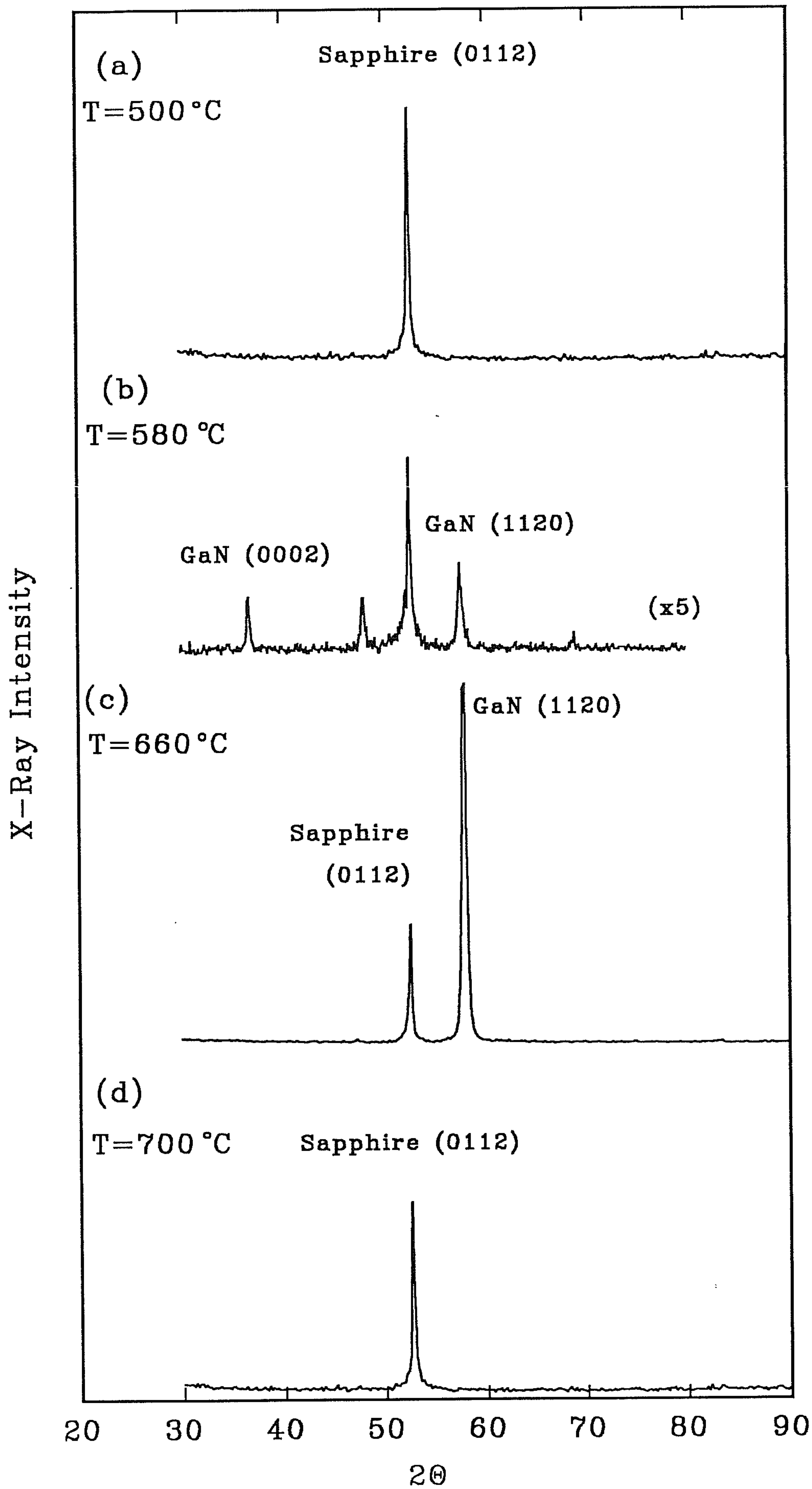
Figure 3. (a) Intensity of (0002) and $(11\bar{2}0)$ GaN x-ray diffraction peaks for films deposited at constant pressure, $N_2$ flow, and various substrate temperatures; and (b) the corresponding film compositions measured by RBS.

Figure 4. (a) Tauc plot for a GaN film grown at 660 °C, 10 mTorr pressure, and 70% $N_2$. The energy axis intercept is the direct optical bandgap. (b) Room temperature photoluminescence spectra of the same film using a HeCd laser. Measured FWHM is 11 meV.



110 W Power
10 mTorr Pressure
660 °C
Growth Rate (Å/s)
N2 Flow (sccm)
0
1
2
3
4
5
0
20
40
60
80
100


Fig 1.



(a)
T=500°C
Sapphire (0112)
(b)
T=580 °C
GaN (1120)
GaN (0002)
(x5)
(c)
T=660°C
GaN (1120)
Sapphire
(0112)
(d)
T=700°C
Sapphire (0112)
X-Ray Intensity
20
30
40
50
60
70
80
90
2Θ


Fig. 2

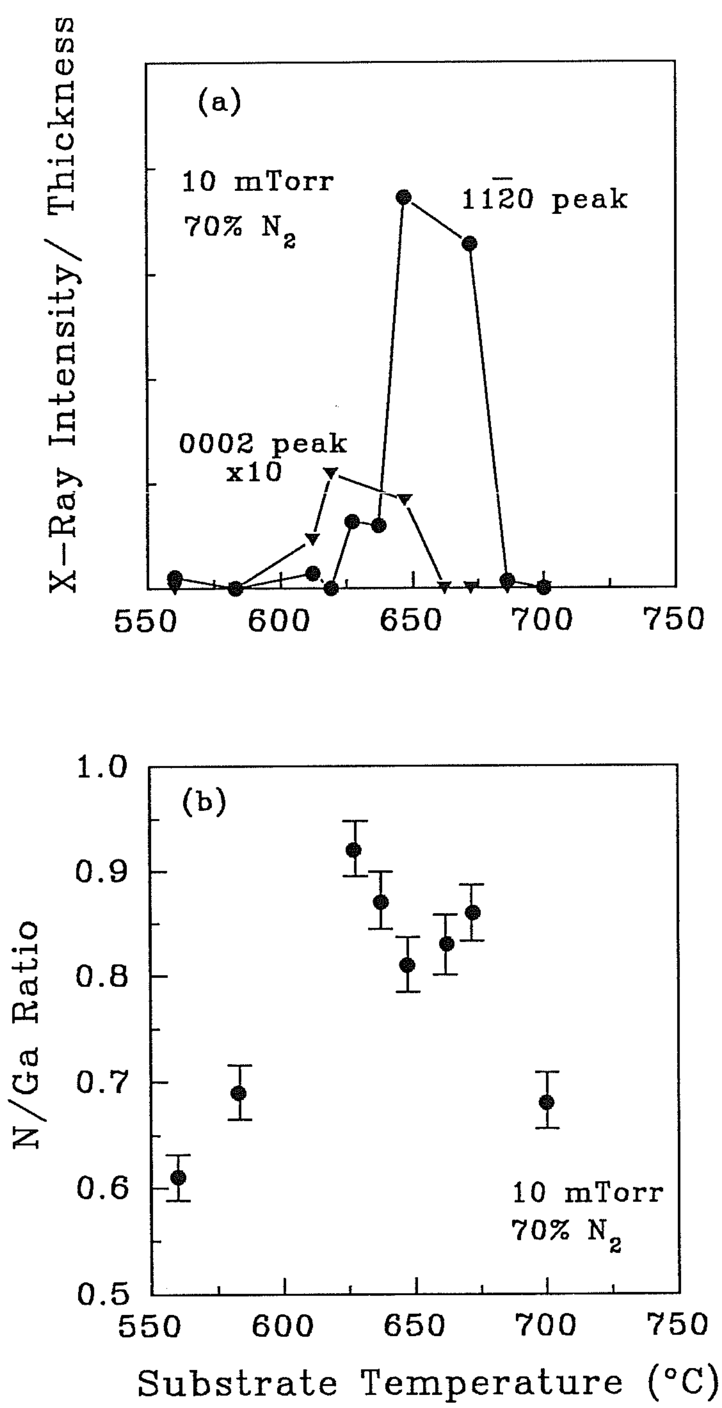
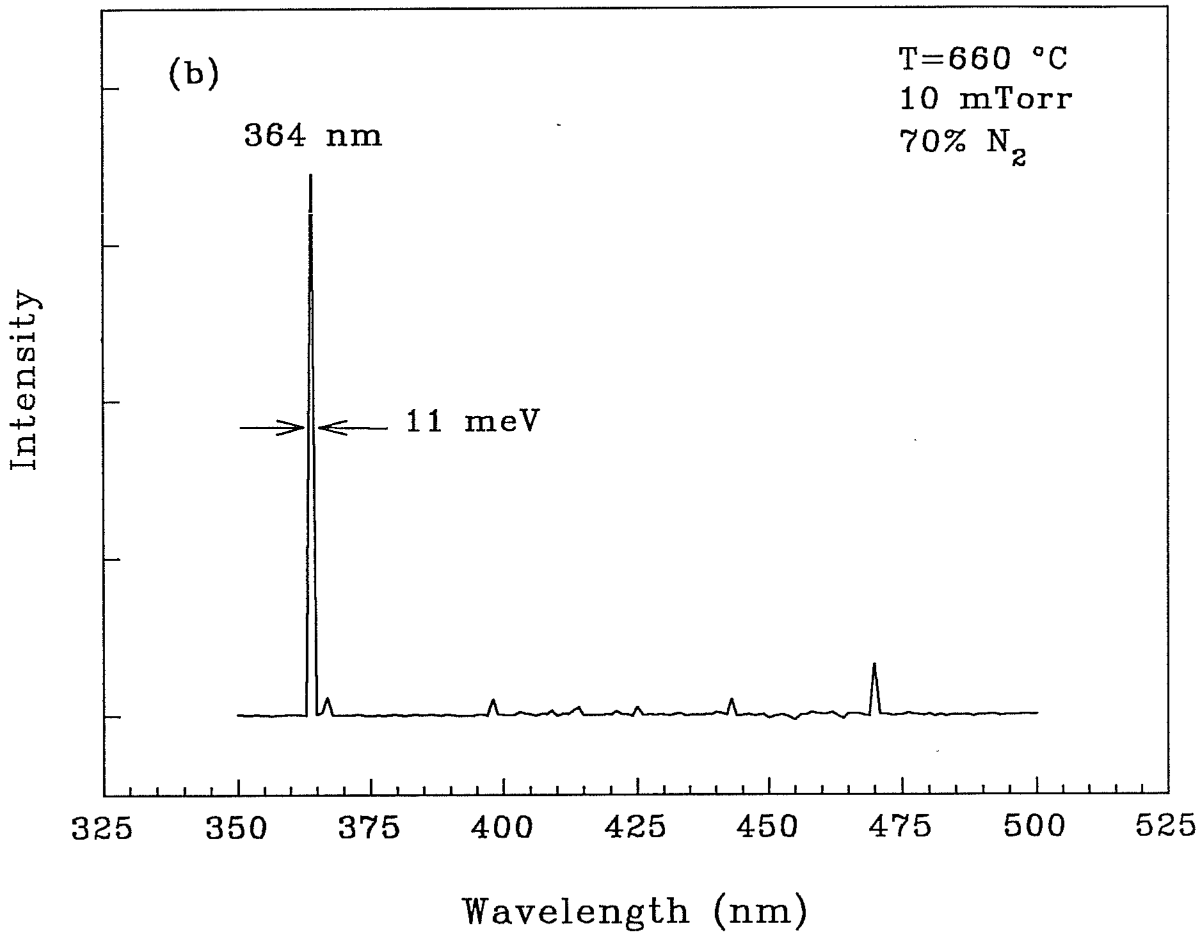

(a)
10 mTorr
70% $N_2$
11$\bar{2}$0 peak
0002 peak
x10
X-Ray Intensity/ Thickness
550
600
650
700
750
(b)
1.0
0.9
0.8
0.7
0.6
0.5
N/Ga Ratio
10 mTorr
70% $N_2$
550
600
650
700
750
Substrate Temperature (°C)

Fig 3



(b)
364 nm
11 meV
T=660 °C
10 mTorr
70% N2
Intensity
325
350
375
400
425
450
475
500
525
Wavelength (nm)

Fig 6