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Single crystal wurtzite GaN on (111) GaAs with AlN buffer layers grown by reactive magnetron sputter deposition

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Abstract

We report the growth conditions necessary for highly oriented wurtzite GaN films on (111) GaAs, and single crystal GaN films on (111) GaAs using AlN buffer layers. The GaN films and AlN buffers are grown using rf reactive magnetron sputter deposition. Oriented basal plane wurtzite GaN is obtained on (111) GaAs at tempertures between 550-620^{o}C. However, using a high tempertaure 200 Å AlN buffer layer epitaxial GaN is produced. Crystal structure and quality is measured using x-ray diffraction (XRD), reflection electron diffraction (RED), and a scanning electron microscope (SEM). This is the first report of single crystal wurtzite GaN on (111) GaAs using AlN buffer layers by any growth technique. Simple AlN/GaN heterostructures grown by rf reactive sputter deposition on (111) GaAs are also demonstrated.

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Introduction

Gallium Nitride is a promising material in the development of short-wavelength light emitting devices (LED) due to its 3.4 eV direct bandgap. However, two principle factors have limited GaN blue LED development: controllable p-type doping, and substrates for epitaxial growth. P-type conduction has now been demonstrtaed in Mg-doped GaN films grown by metal-organic chemical vapor deposition (MOCVD), and can be enhanced using low energy electron beam irradiation [1,2]. Neither bulk GaN or AlN crystals are yet available, therefore alternate substrates must be used. Large lattice and thermal expansion differences between GaN and the substrate create interface strain and dislocations which will degrade p-n junction performance. GaN is typically grown on sapphire substrates despite a 16% lattice mismatch. Attempts on other substrates include: silicon [3-7], gallium arsenide [3,8-14], gallium phosphide [3], silicon carbide [15-17] and magnesium oxide [18]. Aluminum nitride has been used effectively by many researchers as a thin-film buffer layer on sapphire for improved GaN growth [19,20]. Table I summarizes the material data for GaN and substrates considered for wurtzite GaN heteroepitaxy. The lattice parameter for the (111) cubic crystals (GaAs,Si) are given as the effective spacing in the (111) plane corresponding to "a" of the wurtzite crystal for easier comparison. Sapphire data is also translated into the wurtzite system.

Despite the large lattice mismatch, GaAs is a desirable substrate due to its large role in the electrooptic industry. If GaN could be grown epitaxially GaAs, device integration would be possible. Zinc-blende crystals in the (111) direction differ from wurtzite basal planes only by the stacking order of their planes. Few researchers have used GaAs as substrates for GaN growth, possibly because early comparisons showed sapphire produced smoother and more oriented GaN films [8]. Cubic GaN, grown by gas-source molecular beam epitaxy (MBE), has been reported on (001) GaAs [9-13]. Recent work in Japan has also shown oriented wurtzite GaN on (111) GaAs using gas-source MBE [9]. However, our films exhibit narrower x-ray diffraction peaks even without the use of an AlN buffer layer.

In this paper we report the growth conditions of highly oriented wurtzite GaN films on (111) GaAs, and single crystal GaN films on (111) GaAs using AlN buffer layers. The GaN films and AlN buffers are grown using rf reactive magnetron sputter deposition. The sensitivity of both substrate temperature and nitrogen partial pressure on the growth of GaN on (111) GaAs is reported. Crystal structure and quality is measured using x-ray diffraction (XRD), reflection electron diffraction (RED), and a scanning electron microscope (SEM). This is the first report of single crystal wurtzite GaN on (111) GaAs using AlN buffer layers by any growth technique. Simple AlN/GaN heterostructures are also demonstrated.

Experimental Procedure

The GaN films were deposited using US Gun-II two-inch modular sources. One target was pure gallium (99.999999%) held in a stainless steel cup. For the AlN buffer layers, a second gun was used with a pure aluminum target (99.9999%). The *n*+ GaAs substrates were degreased and etched in a <111> directional etch of H_2O:5 H_2SO_4: H_2O_2 for 2 minutes before deposition. The chamber was evacuated to less than 10^{-7} Torr, and then backfilled with a mixture of N_2 and Ar gas to 25 mTorr. The substrates were heated from 500-700^{o}C as measured by a thermocouple clamped to the surface of the heating block. The GaAs substrates were ion etched in the chamber with a 2.0 KV argon ion beam for 15 minutes prior to deposition. The growth rate was measured by a quartz-crystal oscillator calibrated with a stylus profilometer. Growth rates varied from 1-5 Å/s. After deposition, the substrates were cooled to 200°C in a 100% nitrogen atmosphere at 100 mTorr. The choice of deposition parameters was partly determined from our earlier work on sapphire substrates [21]. Higher partial pressures of nitrogen (25 mTorr) were needed to crystallize GaN on (111) GaAs than for sapphire (10 mTorr). Table II summarizes the conditions used for the single crystal GaN films, and for the AlN buffer layer.

Results and Discussion

The GaN film's crystal orientation was analyzed using a Siemens x-ray diffractometer (CuKα, λ=0.154 nm). For temperatures below 550°C only mixed phases of GaN were obtained as shown in the two-theta x-ray diffraction pattern in Figure 1a. In this temperature range, the GaN films were characterized by rough surfaces when viewed with a high-power optical microscope (100x). However, within a narrow temperature range (580-620° C), highly oriented wurtzite basal plane GaN was achieved with an optically smooth surface. Figure 1b shows the x-ray diffraction pattern of a 1 μm GaN film grown directly on (111) GaAs using the conditions listed in Table II. Both the (0002) peak at 2Θ=34.607° and the (0004) peak at 2Θ=72.99° are observed. The (0002) peak corresponds to d-spacing of 2.589 Å, and the (0004) to 1.295 Å, which yields a basal plane spacing of 5.178 and 5.180 Å, respectively. The measured plane spacing agrees well with the theoretical value of 5.182 Å. The full-width-at-half-maximum (FWHM) of the (0002) GaN peak in Figure 1b is 10 minutes. For films grown under similar conditions but ranging in thickness from 0.5-4.0 μm , no variation in peak location or peak width was measured, although the (0004) peak was not visible for all cases. Reflection electron diffraction (RED) was used to verify the wurtzite symmetry, since cubic GaN growing in the (111) direction could display a similar x-ray diffraction pattern.

For the GaN films grown on (111) GaAs under the conditions in Table II, the film's surface appear completely smooth when observed through a high-power optical microscope(100x). However, a scanning electron microscope (SEM) picture shown in Figure 2a reveals the granular nature of a 1 μm thick GaN film. These grains are 150-200 nm in diameter with the c-axis parallel to the <111> GaAs substrate, but they lack in-plane orientation.

In an attempt to increase the in-plane orientation, a high-temperature AlN buffer layer was deposited on the (111) GaAs substrates using the growth conditions for AlN in Table II. Many researchers have demonstrated that AlN buffers on sapphire substrates greatly enhance GaN quality [18,19]. We find this to be true for (111) GaAs substrates as well. The buffer layer serves to greatly reduce the lattice strain between the substrate and GaN film in addition provides nucleation sites for GaN growth. A SEM picture of a 1 μm GaN film on (111) GaAs with a 200 Å thick AlN buffer layer is shown in Figure 2b. Grains are no longer visible and the x-ray diffraction is similar to figure 1b with a (0002) GaN peak FWHM of 9 minutes at $2\Theta = 34.598^{o}$. No x-ray diffraction peaks corresponding to (0002) AlN were visible for the 200 Å buffer layer, however, peaks were observed for thicker AlN layers as described below. There is a distinct terracing present in the GaN films in Figure 2b with step widths of 1-1.2 μm. We suspect the terracing is a result of the grain size and orientation of the AlN layer, but extensive modeling of AlN growth on the (111) GaAs face is needed to speculate further. Buffer layers less than 100 Å did not have a measurable effect on improving the in-plane orientation of the GaN layer.

Thicker AlN layers and AlN/GaN heterostructures were grown on (111) GaAs using the conditions listed in Table II. The cross-sectional SEM and x-ray diffraction pattern for an AlN/GaN/AlN structure are shown in Figure 3a and 3b. The GaAs was cleaved and partially separated from the AlN/GaN/AlN layers when preparing the cross-sectional view. The structure consists of a 50 nm GaN layer (white center section) sandwiched between two 250 nm AlN layers. Figure 3a shows the basal plane AlN peak located at $2\Theta = 36.104^0$ with a FWHM of 18 min. The measured plane spacing is therefore 4.972 Å which agrees with accepted value of 4.980 Å. The GaN layer is only 50nm thick yet its peak at is still observed at 34.60^0.

For growth temperatures greater than 640^0C, the (0002) GaN x-ray diffraction peaks vanish and many films delaminated from the GaAs substrates. We found the delamination could be minimized and in some cases eliminated if the GaN films were cooled slowly from the growth temperature (~100^0/hr). Also at temperatures above 600^0C the GaAs substrates start to degrade. This degradation, caused by the evaporation of arsenic, could be taken advantage of by attempting to replace the top several monolayers of arsenic with nitrogen before deposition of the GaN film, thus creating a pseudo-GaN substrate. We are currently investigating this possibility.

Conclusion

For temperatures greater than 640^0C, strain encountered upon cooling, due to the large difference in thermal expansion coefficient and lattice constant, causes films to delaminate, and for temperatures less than 560^0C GaN does not crystallize at all. But, within a narrow temperature range (580-620^0C), GaN grown directly on (111) GaAs is highly oriented in the c-plane but lack inplane uniformity. A 200 Å thick, high-temperature AlN layer dramatically enhances the in-plane orientation, producing single crystal GaN.

Acknowledgments

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Material	Lattice constant (Å)	a_{GaN}-a_{sub}-/a_{sub} (%)	Thermal exp. coef. (x10 $^{-6}$/K)	α_{GaN}-α_{sub}-/α_{sub}
GaN	a=3.189	----	5.6	----
	c=5.182	----	3.2	----
AlN	a=3.111	+2.5	4.2	+33.3
	c=4.980	+4.1	5.3	-39.6
α - SiC (6H)	a=3.080	+3.5	4.2	+33.3
	c=15.11	-65.7	4.8	-33.3
Al_2O_3	a=2.740	+16.3	7.5	-25.3
	c=12.991	-60.10	8.5	-62.3
GaAs (111)	a=3.997	-20.2	6.0	-6.6
Si (111)	a= 3.839	-16.9	3.6	+55.5

Table I. Lattice paramters and thernal expansion coefficients for potential substrates for wurtzite GaN heteroepitaxy. All lattice parameters are given in the wurtzite system.

Film type	GaN	AlN buffer
Growth Temperature	580 °C	580 °C
Chamber Pressure	25 mTorr	25 mTorr
N_2:Ar ratio	7:3	7:3
N_2 flow rate	200 sccm	200 sccm
Target-to-substrate distance	6.5 cm	6.5 cm
RF Power	110 W	200 W
Growth rate	4.0 Å/s	1.0 Å/s

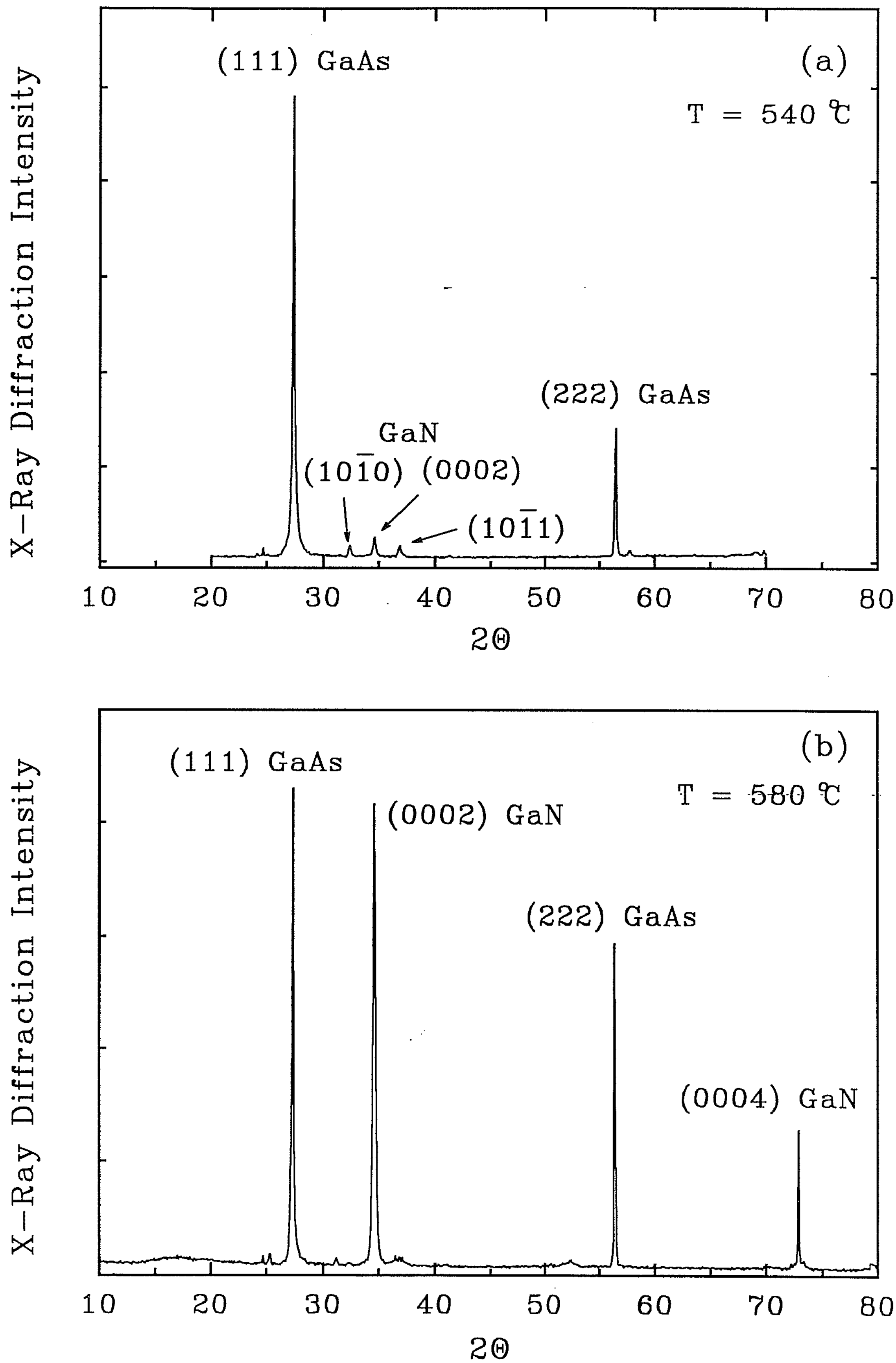
Table II. Growth conditions for highest crystalline quality GaN films on(111) GaAs substrates, and for the AlN buffer layer.

Captions

Figure 1. X-ray diffraction pattern for a 1μm GaN film grown directly on (111) GaAs at (a) 550 ^oC, and (b) 580 ^oC. Wurzite GaN peaks corresponding to the (0002) and (0004) reflections are observed only for growth temperatures between 580-620 ^oC.

Figure 2. Surface morphology of 1μm GaN film grown (a) directly on (111) GaAs, and (b) with a 200 Å AlN buffer on (111) GaAs taken with scanning electron microscope. All layers grown at 580 ^oC.

Figure 3. (a) Cross-sectional view of AlN/GaN/AlN heterostructure on (111) GaAs, and (b) X-ray diffraction pattern of heterostructure indicating AlN and GaN basal plane spacing of 4.972 Å and 5.180 Å respectively.



(111) GaAs
(a)
T = 540 ℃
(222) GaAs
GaN
(10$\bar{1}$0) (0002)
(10$\bar{1}$1)
X-Ray Diffraction Intensity
10 20 30 40 50 60 70 80
2Θ
(111) GaAs
(b)
T = 580 ℃
(0002) GaN
(222) GaAs
(0004) GaN
X-Ray Diffraction Intensity
10 20 30 40 50 60 70 80
2Θ

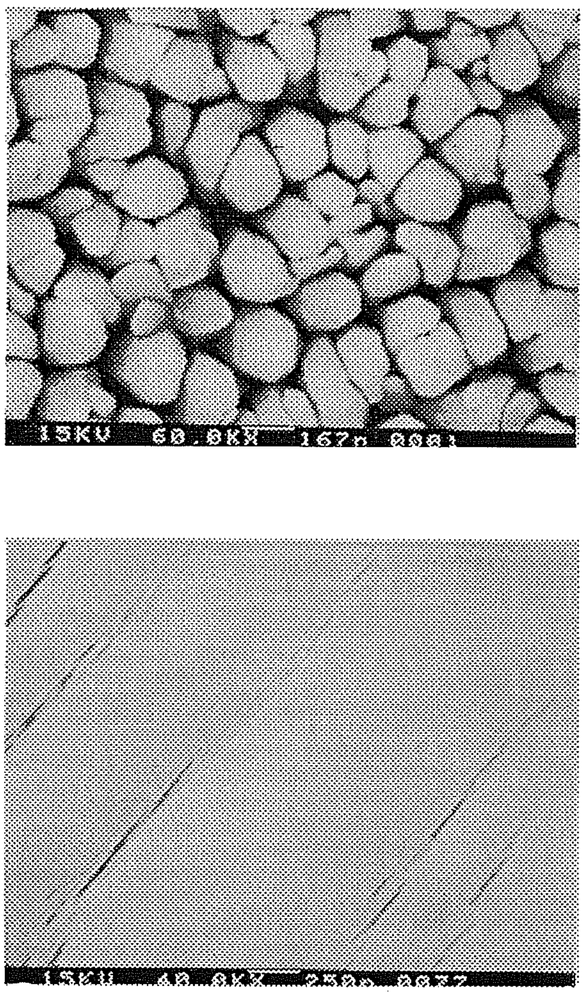


Figure 2a,b

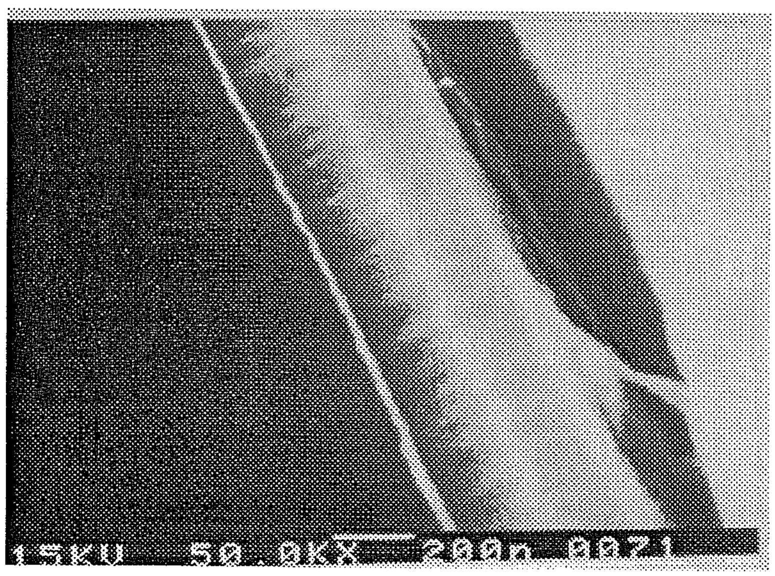
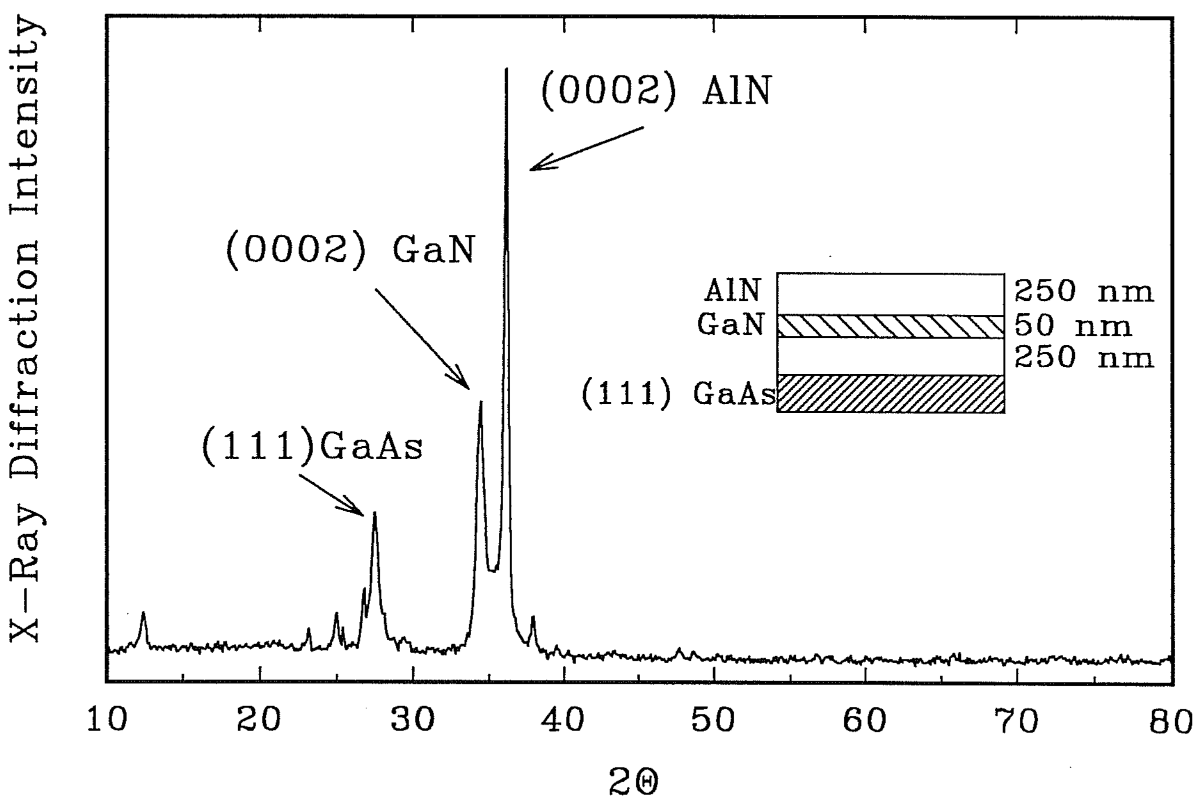


Figure 3a



X-Ray Diffraction Intensity
(0002) AlN
(0002) GaN
(111)GaAs
AlN
GaN
(111) GaAs
250 nm
50 nm
250 nm
10
20
30
40
50
60
70
80
2Θ

Figure 3b