# Quarterly Technical Report

## Selected Energy Epitaxial Deposition and Low Energy Electron Microscopy of AlN, GaN and SiC Thin Films

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**13. ABSTRACT** *(Maximum 200 words)*

The stoichiometry and the atomic and electronic structure of the anion and cation terminated (0001) surfaces of GaN and AlN are being investigated using the multicenter tight-binding formalism. The surfaces are described within the slab-supercell formalism. Results show that an unreconstructed (1×1) surface is highly unstable with respect to surface reconstructions that change the surface stoichiometry of the outermost layers and, therefore, stabilize the atomic structure and eliminate the surface polarity. Growth of stoichiometric and smooth AlN and GaN thin films on Si(l00) and off-axis 6H-SiC(0001) has been achieved using a seeded supersonic molecular beam under conditions suitable for observation in the low energy electron microscope (LEEM). An arc heated N source is being currently tested for intensity and beam composition. Films of GaN have also been achieved on sapphire substrates using a new multichamber selected energy epitaxy deposition (SEED) system. *In situ* RHEED and SEM results show the films to have good morphology. Mass selected, essentially monoenergetic and chemically pure $N_2^+$ and $N^+$ ions beams with energies of ~20 eV and FWHM ~1 eV and useful for nitride film deposition were extracted from the Colutron ion-beam systems.

**14. SUBJECT TERMS**
GaN, AlN, thin films, atomic structure, electronic structure, anion terminated surface, cation terminated surface, tight-binding formalism, slab-supercell formalism, surface stoichiometry, growth, supersonic molecular beam, N source, RHEED, SEM, Colutron, N beams

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# I. Introduction

The realized and potential electronic applications of AlN, GaN and SiC are well known. Moreover, a continuous range of solid solutions and pseudomorphic heterostructures of controlled periodicities and tunable bandgaps from 2.3 eV (3C-SiC) to 6.3 eV (AlN) have been produced at North Carolina State University (NCSU) and elsewhere in the GaN-AlN and AlN-SiC systems. The wide bandgaps of these materials and their strong atomic bonding have allowed the fabrication of high-power, high-frequency and high-temperature devices. However, the high vapor pressures of N and Si in the nitrides and SiC, respectively, force the use of low deposition temperatures with resultant inefficient chemisorption and reduced surface diffusion rates. The use of these low temperatures also increases the probability of the uncontrolled introduction of impurities as well as point, line and planar defects which are likely to be electrically active. An effective method must be found to routinely produce intrinsic epitaxial films of AlN, GaN and SiC having low defect densities.

Recently, Ceyer [1, 2] has demonstrated that the barrier to dissociative chemisorption of a reactant upon collision with a surface can be overcome by the translational energy of the incident molecule. Ceyer's explanation for this process is based upon a potential energy diagram (Fig. 1) similar to that given by classical transition-state theory (or activated-complex theory) in chemical kinetics. The dotted and dashed lines in Fig. 1 show, respectively, the potential wells for molecular physisorption and dissociative chemisorption onto the surface. In general, there will be an energy barrier to overcome for the atoms of the physisorbed molecule to dissociate and chemically bond to the surface. Depending upon the equilibrium positions and well depths of the physisorbed and chemisorbed states, the energy of the transition state $E^*$ can be less than zero or greater than zero. In the former case, the reaction proceeds spontaneously. In the latter case, the molecule will never proceed from the physisorbed state (the precursor state) to the chemisorbed state unless an additional source of energy can be drawn upon to surmount the barrier. This energy can only come from either (1) the thermal energy of the surface, (2) stored internal energy (rotational and vibrational) of the molecule, or (3) the incident translational kinetic energy of the molecule. Conversion of translational kinetic energy into the required potential energy is the most efficient of these processes. Moreover, by adjusting the kinetic energy, Ei, of the incoming molecule, it is possible to turn off the reaction ($Ei < E^*$), to tailor the reaction to just proceed ($Ei = E^*$), or to set the amount of excess energy to be released ($Ei > E^*$). The thrust of the present research is to employ these attributes of the beam translational energy to tune the reaction chemistry for wide bandgap semiconductor epitaxial growth.

The transition state, $E^*$, is essentially the activation energy for dissociation and chemisorption of the incident molecules. Its exact magnitude is unknown, but is most certainly

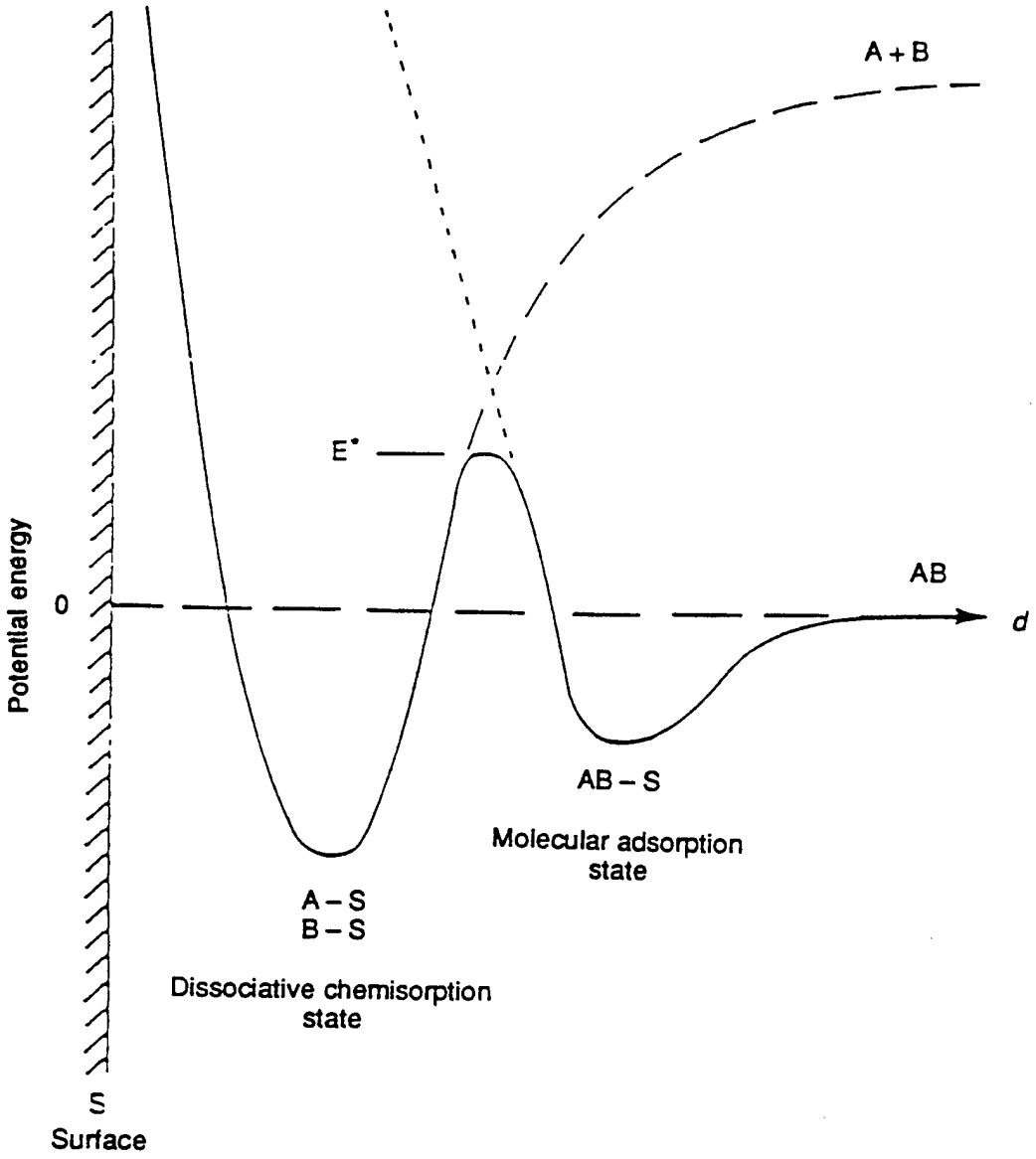


Figure 1. Schematic potential energy diagram of an activated surface reaction involving a molecularly physisorbed precursor state [from Ref. 1].

lower than the dissociation energy of the free molecule. It does not necessarily follow, however, that any kinetic energy above E* will promote high-quality epitaxial growth of GaN. One must take into consideration another energy threshold, Ed, beyond which the kinetic energy of the incident flux will cause damage to the epitaxial film being synthesized. A typical Ed threshold value is approximately five times the bandgap of the crystal and in the case of GaN, Ed ≈18 eV.

From the above consideration, it is clear that the key to high quality epitaxial growth is to be able to tune the energy of the incoming flux species over a range of energies defined by the window between E* and Ed. Since the window is quite restrictive, i.e. 1-20 eV, it is essential

that the energy spread of the flux species must be small, i.e. the flux species should ideally be monoenergetic. To this end, we employ Selected Energy Epitaxial Deposition (SEED) systems for the growth of AlN, GaN and SiC wide bandgap semiconductors. The SEED systems are of two types: (1) a seeded-beam supersonic free-jet (SSJ) and (2) a dual ion-beam Colutron. Both these SEED systems have the desirable property of a narrow energy spread of $\leq 1$ eV.

Epitaxial growth using the seeded-beam SSJ involves a close collaboration between investigators at NCSU and Arizona State University (ASU). At ASU, the SSJ is interfaced directly into a low-energy electron microscope (LEEM) for the conduct of *in situ* studies of the nucleation and growth of epitaxial layers; while at NCSU, the SSJ systems are used to grow device-quality AlN, GaN and SiC for real applications. Exchanges in personnel (students) and information between the two groups ensures the achievement of desired results. The additional thin film growth experiments using dual-beam Colutrons and the theoretical studies referred to in this report are primarily conducted at ASU.

The research conducted in this reporting period and described in the following sections has been concerned with (1) the investigation of the stoichiometry and the atomic and electronic structure of the anion and cation terminated (0001) surfaces of GaN and AlN using the multicenter tight-binding formalism, (2) the growth of stoichiometric and smooth AlN and GaN thin films on Si(100) and off-axis 6H-SiC(0001) substrates, (3) the growth of GaN films on sapphire substrates using a new multichamber selected energy epitaxy deposition (SEED) system, and (4) the extraction of mass selected, essentially monoenergetic and chemically pure $N_2^+$ and $N^+$ ion beams from Colutron ion-beam sources. The following individual sections detail the procedures, results, discussions of these results, conclusions and plans for future research. Each subsection is self-contained with its own figures, tables and references.

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## II. *Ab initio* Calculation of the Structure and the Growth Properties of the III-V Nitrides

Within the generalized tight-binding approach [1], we are able to reproduce measured lattice constants and phonon frequencies of zincblende and wurtzite GaN and AlN with an accuracy which is comparable to that of highly converged *ab initio* calculations. Additionally, molecular dynamics simulations performed for the $(10\bar{1}0)$ and $(11\bar{2}0)$ surfaces of hexagonal-phase GaN demonstrate that the multicenter tight-binding scheme allows us to compute the surface energy and relaxation of nonpolar group-III nitride surfaces with similar success. As an example, the bond length contraction of 7.9 percent and the bond rotation of 7.8° calculated for the $(10\bar{1}0)$ surface, as well as the energy differences determined for stoichiometric and non-stoichiometric surface compositions are in excellent agreement with the theoretical investigations of Refs. [2] and [3]. Similar agreement is achieved for GaN$(11\bar{2}0)$.

To check the applicability of the tight-binding formalism to polar semiconductor surfaces, simulations have been performed for GaAs which represents the best understood compound semiconductor. The results obtained for the reconstruction of the cation and anion terminated (111) surfaces agree very well with previous experimental and theoretical investigations [4, 5].

On the basis of such numerous and careful tests of the method, reliable predictions are expected to be obtained for the atomic geometry and possible reconstructions prominent in the (0001) surfaces of hexagonal GaN and AlN. Very recently, the formation of a $p(2\times2)$ reconstruction pattern occurring during molecular beam epitaxy has been reported [6]. Currently, calculations are focused on the comparison of the total energy and electronic structure of a large variety of different atomic geometries and surface compositions. The unreconstructed $(1\times1)$ surface is found to be highly unstable with respect to the formation of surface reconstructions that change the surface stoichiometry stabilizing the atomic structure by eliminating surface polarity. Energetically stable bonding units are identified that may be responsible for the reconstruction in GaN and other nitride compounds. A thorough analysis of the surface structure is an important prerequisite for future simulations of collision processes.

Analogous to the surface, modifications of the stoichiometry by atomic mixing are expected to eliminate charge accumulation and dipole fields at the interface between 6H-SiC and wurtzite AlN [7]. Molecular-dynamics simulations will be performed in order to study in more detail the atomic and electronic structure of the AlN/SiC interface.

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# II. Deposition of GaN and AlN Thin Films on Si(100) and 6H-SiC(0001) Using a $NH_3$ Seeded He Supersonic Molecular Beam Source

## A. Introduction

The nitride family of AlN, GaN and InN thin films have shown to be strong candidates for electronic and optoelectronic applications. With direct band gaps of 6.2 eV, 3.4 eV and 1.9 eV for AlN, GaN and InN respectively, solid solutions based on these materials provide for band gap modifications suitable for applications ranging from the red to the deep UV region of the spectrum [1]. Due to the high bond strength between N and H in $NH_3$, the growth of III-V nitrides requires high substrate temperatures unless some other form of activation is present. Supersonic molecular beam epitaxy (SMBE) has been shown to enhance the surface decomposition of silane and methane [2, 3] because of the possibility of tuning the kinetic energy of these species to deform and cleave the bonds upon impact with the substrate. In addition, the tuning of the energy spread is possible with SMBE. This is important in order to experimentally determine the chemisorption barriers for the systems being studied, as well as to provide species with high sticking coefficients at high enough intensities. Supersonic molecular beam epitaxy is, therefore, a useful technique for the low temperature growth of single-crystalline GaN films at suitable growth rates using $NH_3$. A review of supersonic molecular beams can be found in Scoles [4].

Deposition of GaN and AlN thin layers on 6H-SiC(0001) using a triply differentially pumped $NH_3$ seeded He supersonic molecular beam source has been demonstrated. Results on the film stoichiometry and surface morphology are presented.

## B. Experimental Procedure

The molecular beam source chamber has been described in previous reports. The source chamber was interfaced with a deposition chamber which houses a sample holder, an isolation valve between the source and the deposition chamber and an Al evaporator. The deposition chamber was pumped by a liquid nitrogen trapped M-4 Varian diffusion pump. The samples were resistively heated by passing a current through them and the temperature was measured using a disappearing filament pyrometer. The temperature of the Al evaporator was also measured with the pyrometer. Growth of AlN on Si(100) was performed at a substrate temperature of 600°C to 1000°C in order to determine the growth conditions that lead to a 1:1 - Al:N stoichiometry. These growth parameters were then utilized to deposit AlN films on SiC substrates. The SiC substrates were n type (1.2E18 $cm^{-3}$), 4° off axis, of the 6H polytype with (0001) orientation. The substrates contained a 0.5 μm epilayer and a 0.5 μm thick oxide layer. The SiC substrates were degreased by rinsing and sonicating in methanol and acetone. After degreasing, the samples were dipped in a 10% HF aqueous solution to remove the oxide.

The samples were then loaded into the deposition chamber which was evacuated and baked until a base pressure < $5\times10^{-9}$ Torr was obtained. A liquid nitrogen trap was then filled to obtain a base pressure < $3\times10^{-10}$ Torr. The filament surrounding the BN crucible containing Al was degassed by heating it until a pressure of $6\times10^{-10}$ Torr was obtained with the filament at 900°C. A similar outgassing procedure was performed on the Ga evaporator. The sample was then degassed by heating to 650°C while the pressure in the chamber was maintained at < $1\times10^{-9}$ Torr. At this point the sample was annealed at 900°C for 20 min. [5]. The sample was then cooled to the deposition temperature (i.e. 600°C-900°C) and AlN deposition was initiated. Gallium nitride deposition was performed after AlN deposition at 900°C. The deposition of GaN was performed at 800°C with a Ga evaporator. After the deposition was completed, the evaporator shutter was closed. The evaporator was turned off, and the sample was progressively cooled in the presence of the $NH_3$ seeded He beam. The samples were then characterized for composition and surface morphology using Rutherford backscattering spectroscopy (RBS), Nomarski optical microscopy, scanning electron microscopy (SEM) and electron channeling. With the $NH_3$ beam intensity at $3\times10^{14}$ $cm^{-2}s^{-1}$, the time taken to deposit the AlN and GaN layers was 60 min each. The stagnation temperature was 300K for a $NH_3$ energy of ≈ 0.22 eV, and the nozzle diameter was 100μm at a stagnation pressure of 940 Torr. The Al flux was measured by evaporating Al onto a glass slide and measuring the Al layer thickness via a Decktak profilometer and RBS. The Al flux varied from 2Å/min. to 10Å/min. depending on the substrate temperature. Preliminary studies on the energy dependence on the GaN film characteristics were performed by increasing the nozzle stagnation temperature to 563K ($NH_3$ energy ≈ 0.42 eV) at a stagnation pressure of 1300 Torr while maintaining the rest of the growth conditions constant. Under the latter stagnation conditions, the $NH_3$ flux was $2.2\times10^{14}$ $cm^{-2}s^{-1}$.

C. Results and Discussion

The Al flux had to be increased in conjunction with increasing substrate temperature in order to maintain stoichiometry and a maximum growth rate of 2.25Å/min (Fig. 1). The growth rate was determined as the estimated layer thickness using RBS, divided by the deposition time. There can be a considerable error in our thickness estimations using RBS, because in the modeling of the thickness the true density of the film is not known. For a given temperature, if the Al flux was greater than that indicated by the line in Fig. 1, the films contained excess Al. If the Al flux was decreased, the AlN growth rate was dramatically reduced. Because the $NH_3$ flux was kept constant as a function of substrate temperature and the film thickness was comparable for the various substrate temperatures under consideration, the amount of N incorporated into the film was the same. Therefore, it is apparent that the beam

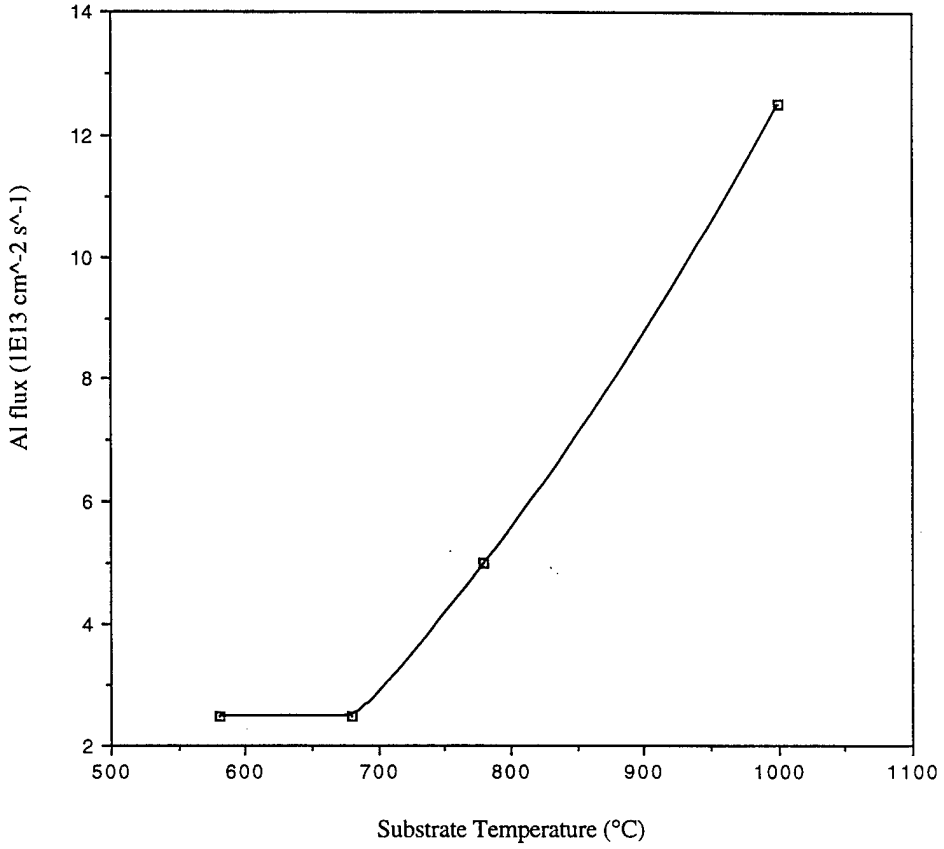


Figure 1. Al flux and substrate temperature used to maintain growth of stoichiometric AlN at 2.25 Å/min.

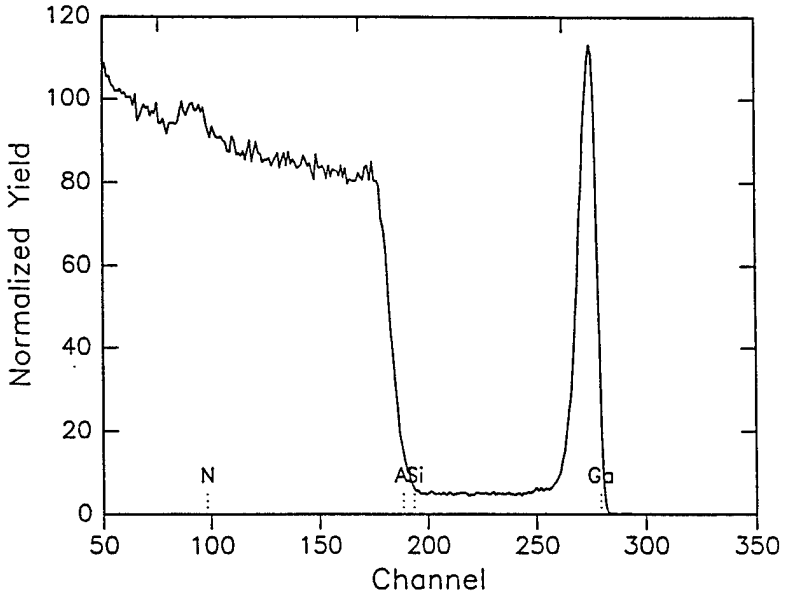


Figure 2. RBS spectra of GaN film grown on Si (100) at 800°C.

kinetic energy is inducing the decomposition of $NH_3$ instead of the substrate temperature. This suggest the existence of a direct dissociative chemisorption pathway [2, 3].

The Ga flux had to be increased with increasing substrate temperature in order to maintain growth of stoichiometric GaN. Figure 2 shows an RBS spectra for a stoichiometric GaN film grown on Si(100) with a $NH_3$ kinetic energy of 0.22 eV. For GaN grown at 0.42 eV (kinetic energy), the $NH_3$ flux was lower while the Ga flux was kept constant. The film was also stoichiometric as determined by RBS, and more homogeneous as examined by the optical microscope. It is possible that the incorporation efficiency of N increased with increasing $NH_3$ kinetic energy which would be expected with a direct dissociative chemisorption channel [2, 3]. However, further analysis of the film thickness is required to make a definite statement on this issue.

The AlN films have a smooth surface with occasional hexagonal holes which are reminiscent of the epilayer on the substrate. Silicon carbide electron channeling patterns were degraded upon AlN deposition. Increasing the deposition temperature from 800°C to 900°C yielded an improved electron channeling pattern.

GaN films on AlN layers show a smooth surface when examined under the optical microscope. Further examination of these films is under way.

The N arc heated jet source has been constructed, installed into the SMBE source chamber and is being tested.

## D. Conclusion

Smooth AlN films have been deposited on Si(100) and off-axis 6H-SiC(0001). Smooth GaN films have been deposited on AlN layers on off-axis 6H-SiC(0001). The deposition rate is controlled by the metal flux.

## E. Future Work

Further characterization of GaN and AlN films via atomic force microscopy and SEM will be performed. The arc heated nozzle will be characterized for flux and composition. The SMBE source chamber will be interfaced with the low energy electron microscope (LEEM).

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# IV. Selected Energy Epitaxial Deposition (SEED) of Gallium Nitride Thin Films

## A. Introduction

Gallium nitride is a wide bandgap semiconductor (Eg=3.4 eV) with great potential for optoelectronics and high-temperature, high-frequency, microelectronics applications. State-of-the-art GaN films ($\leq 10^8$ defects per $cm^2$) have been used to fabricate blue light emitting diodes (LEDs) and laser diodes. Moreover, GaN forms a continuous range of solid solutions with AlN (6.28 eV) and InN (1.95 eV), permitting the fabrication, via bandgap engineering, of laser diodes with tunable emission frequencies from covering the visible and UV regions.

Heteroepitaxial growth of high-quality monocrystalline GaN films has been problematic due to the lack of suitable lattice-matched substrate and the thermodynamic instability of GaN under high-temperature chemical vapor deposition (CVD) conditions. Sapphire, the most common substrate, exhibits a 16% lattice mismatch at the GaN(0001)/sapphire(0001) interface; moreover, the thermal expansion coefficient of sapphire is 25% greater than that of GaN. Only by employing a low-temperature AlN or GaN buffer layer can one obtain monocrystalline films on sapphire with defect densities in the $10^8$-$10^9$ $cm^{-2}$ range.

Substrate temperatures in excess of 1000°C are required fro growth of monocrystalline GaN films by halide or metal-organic CVD using $NH_3$. Substrate thermal energy is required to overcome the activation barriers for dissociative chemisorption of $NH_3$ and adatom surface migration (lateral diffusion). Such high growth temperatures are undesirable as GaN is thermally unstable above 620°C *in vacuo* [1]. Plasma-assisted processes have been utilized to lower the GaN growth temperature to approximately 700°C, but ion-induced damage and oxygen contamination are often observed.

The use of energetic neutral beams of precursor molecules is an alternative approach to the epitaxial growth of GaN films at lower substrate temperatures. In selected energy epitaxy (SEE), heavy reactant molecules are seeded in a supersonic expansion of light molecules and thereby accelerated to hyperthermal energies. The precursor molecules attain kinetic energies on the order of several eV which can provide the necessary energy for activating surface processes, such as dissociative chemisorption and adatom migration. Hence, in prospect, monocrystalline GaN films may be grown at much lower substrate temperatures by SEE than by conventional thermal techniques [2]. Moreover, energetic neutral beams with narrow energy distributions are useful in fundamental studies of wide bandgap semiconductor growth using *in-situ* low-energy electron microscopy (LEEM) and other techniques.

As discussed in previous reports (Sept. 1995, Dec. 1995, Mar. 1996), GaN thin films have been deposited at 600°C via SEE by impinging free jets of $NH_3$+He and TEG+He onto sapphire (0001) using V/III ratio $\geq$200. From these results, it is evident that incident

translational energies of the precursors, $NH_3$ and thiethylgallium (TEG), in the hyperthermal regime do influence GaN growth kinetics and film morphology. However, a two-step growth sequence involving low-temperature deposition of a buffer layer followed by growth at higher temperatures was required to achieve smooth, highly-oriented GaN films on sapphire (0001).

In order to fully employ the advantages of SEE, however, well collimated supersonic beams should be used to achieve accurate controllability of growth, and for fundamental investigations. As such, as described in previous reports (June 1996, Sept. 1996), a multi-chamber SEED system has been built. In addition, to study the initial growth processes under or through vacuum, a RHEED (reflected high energy electron diffraction) unit was equipped on the deposition chamber and an XPS analysis unit was connected to the deposition chamber.

In this report, we report our first successful results of GaN growth on sapphire(0001) substrates using the new built multi-chamber system. Film characterization by RHEED, XPS, and SEM is also presented.

B. Experimental Procedure and Results

The SEED/XPS multi-chamber system described in previous report (June, 1996) has been used for GaN growth, and for RHEED observation and XPS analysis. The geometric arrangement of the dual supersonic beams relative to the substrate position is shown in Fig. 1. The TMG( trimethylgallium) and $NH_3$ nozzles were made from stainless steel and contain replaceable laser-drilled orifices. A 240-W cable heater was used to heat each nozzle. The orifices used on the TMG and $NH_3$ nozzles were 50 and 150 μm, respectively. The conical skimmers used for extracting TMG and $NH_3$ beams from supersonic free jets have an opening of 1 mm in diameter, a base of 20 mm in diameter, an included angle of 25° at the opening and

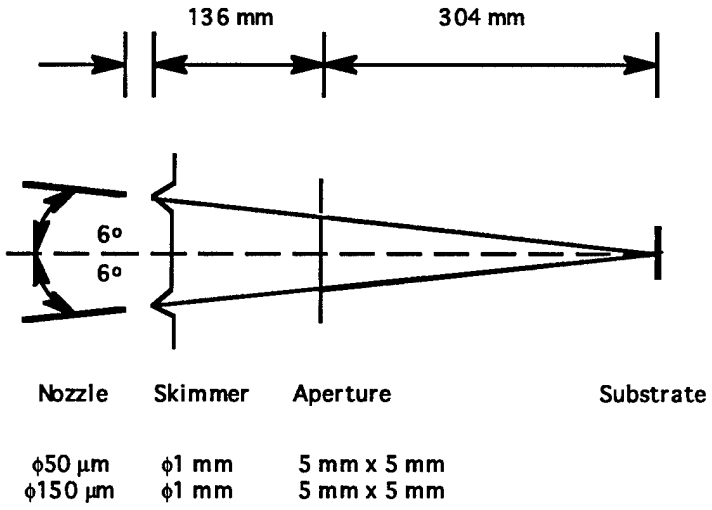



Figure 1. Geometry of TMG(upper) and $NH_3$(lower) supersonic beams incident to the substrate.

of 70° at the base, and a height of 17 mm. The collimation apertures (either 10×10 $mm^2$ or 5×5 $mm^2$) square were located downstream between the 2nd differential pumping stage and the growth chamber. The two molecular beams are directed to the substrate with incident angles of 6°. The deposition area on the substrate was estimated to be 15×15 $mm^2$ with a collimation aperture of 5×5 $mm^2$, and deposited films showed the nearly same areal coverage.

The nozzle-to-skimmer distances were adjusted to obtain reasonable fluxes for GaN growth. With a fixed nozzle-to-skimmer distance, beam fluxes and other characteristics of $NH_3$ and TMG seeded supersonic beams were controlled by adjusting the gas composition ratio and stagnation pressure of each nozzle. $NH_3$ was diluted by He to provide a specific mole ratio and stagnation pressure at given total flow rate. TMG was transported by a flow of He carrier gas passing through the TMG bubbler. The TMG nozzle stagnation pressure was controlled by the total flow rate of He carrier gas and a second He stream which bypassed the TMG bubbler. The mole fraction of TMG in the nozzle is determined by TMG vapor pressure to stagnation pressure ratio. The gas composition was adjusted by either changing bubbler temperature or by adjusting the flow rate of helium bypassing the TMG bubbler.

Shown in Fig. 2 and Fig. 3 are mass spectra of TMG and $NH_3$ seeded supersonic beams measured by a Hiden 301 quadrupole mass spectrometer. The stagnation pressures in TMG and $NH_3$ nozzles were 210 and 480 Torr, respectively. The temperatures of TMG and $NH_3$ nozzles were 35°C and 230 °C, respectively. Peaks at masses of 115(TMG), 100(DMG), 85(MMG), 70(Ga) and 15(methyl radical) which are cracking fragments of TMG, and peaks at masses of 17($NH_3$), 16($NH_2$) and 15(NH) which are cracking fragments of $NH_3$ are clearly seen.

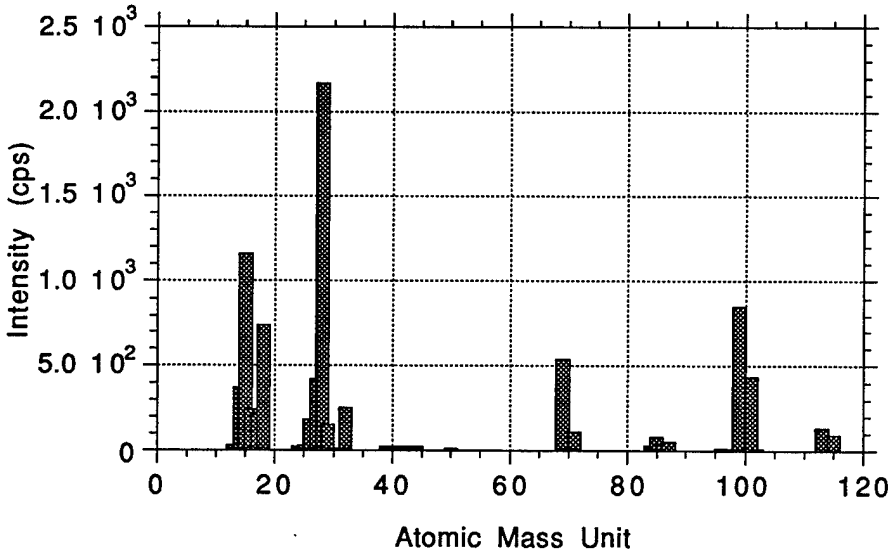



Figure 2. Mass spectrum of TMG-seeded supersonic beam.

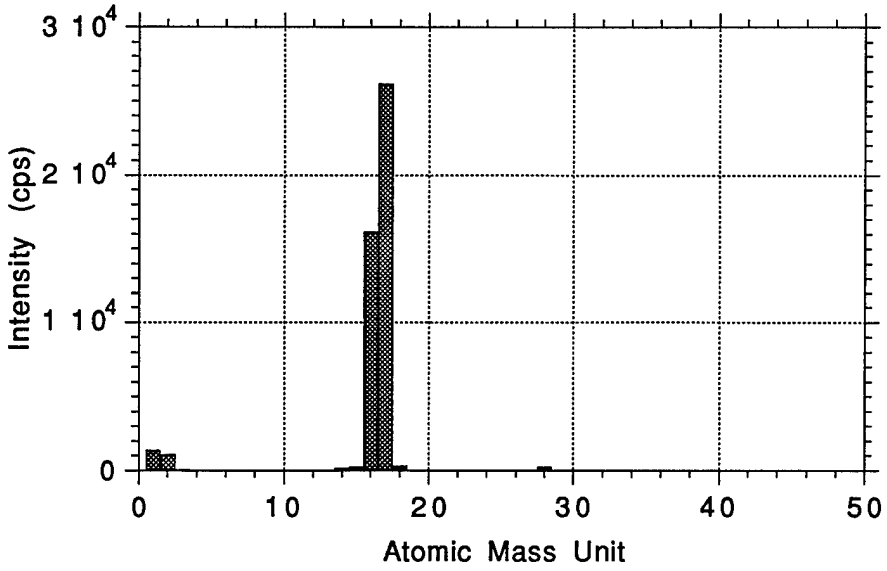



Figure 3. Mass spectrum of $NH_3$-seeded supersonic beam.

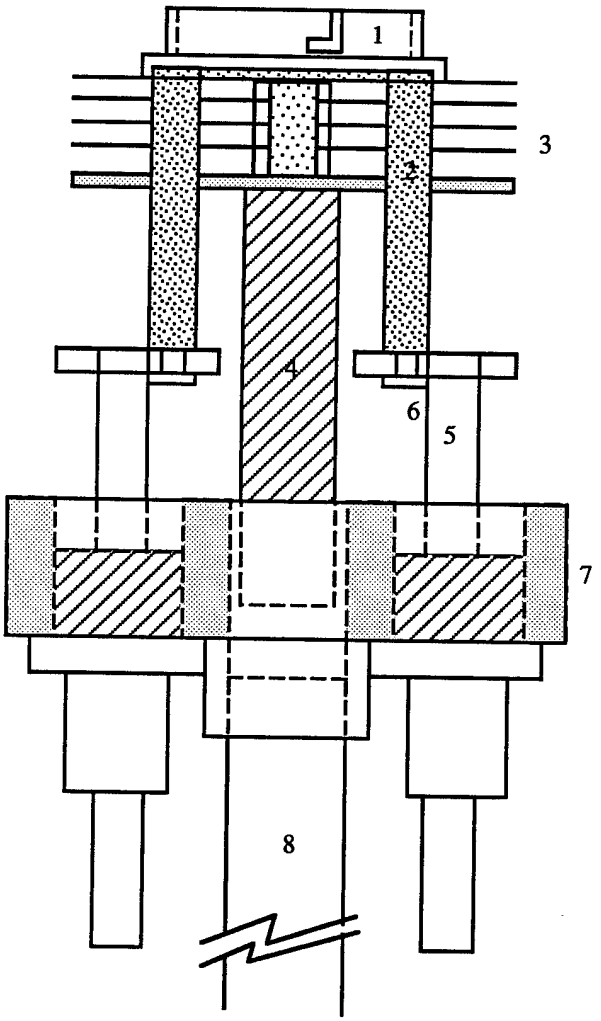
Sapphire substrates for GaN growth were cleaned using the following procedure: 10-min ultrasonic degreasing in trichloroethylene, 10-min etching in 1:1 $H_3PO_4$:$H_2SO_4$ at 80°C, 5-min treatment in 10% aqueous HF, and drying in flowing dry nitrogen. The substrate was supported on a large piece of Si that was mounted in a 30-mm stainless steel holder when quartz lamp heating assembly was used; the substrate was directly placed on a solid Mo holder when the new BN-coated graphite heater assembly (Fig. 4) was used. The substrate holder was transferred into the deposition chamber via a loadlock chamber and a transfer chamber. The loadlock chamber was evacuated by an Alcatel Drytel pump while the transfer chamber was evacuated by a cryopump.

Prior to growth, the substrate holder was firstly heated to 600°C (or 800°C) and maintained 1 hr at the same temperature for degassing. Then, the substrate was exposed to $NH_3$ seeded supersonic beam for 30 minutes to nitride the sapphire substrate.

After the substrate temperature was subsequently lowered to 500°C, the growth of GaN was started by directing TMG-seeded supersonic beam to the substrate. After 1-hr growth (nucleation) at 500°C, the substrate temperature was then raised to 600°C and growth was continued for 4 hours.

C. Results and Discussion

*Substrate Surface Structure after Degassing and Nitridation.* RHEED patterns from sapphire substrate after 1-hr heating at 600°C usually show some streaks with a relatively bright background. A small carbon XPS signal as well as Al and O signals are observed from the sapphire substrate.




1. Bayonet-type coupler
2. Heating Element (PBN-Coated Graphite)
3. Heat Shields (Molybdenum)
4. Connecting Rod (Macor)
5. Electric Feedthrough (Copper)
6. Mo Screw & Cu piece for electrical contact with the feedthrough
7. Connecting Piece (Stainless Steel)
8. Transfer Rod

Figure 4. New substrate heater assembly. The heater is made from BN-coated graphite, and can heat the substrate to 900°C or higher.

After the substrate was further exposed to $NH_3$ seeded supersonic beam at the same temperature, clearer RHEED pattern with sharp streaks were observed. Moreover, less carbon atoms were observed by XPS.

These results indicate that the sapphire substrate after the above successive treatments had a clean and smooth surface.

Characterization of grown GaN by RHEED and XPS. Figure 5 shows XPS spectra taken from samples listed in Table I. As helium flow rate was increased from 5 sccm (Sample #1) to 10 sccm (Sample #2), or as the TMG flux was increased, Ga and N signals increased accordingly, showing the increase of film thickness. As TMG flux was further increased by increasing TMG bubbler temperature from -19°C (Sample #1 and Sample #2) to -10°C (Sample #3), similar XPS spectrum was obtained.

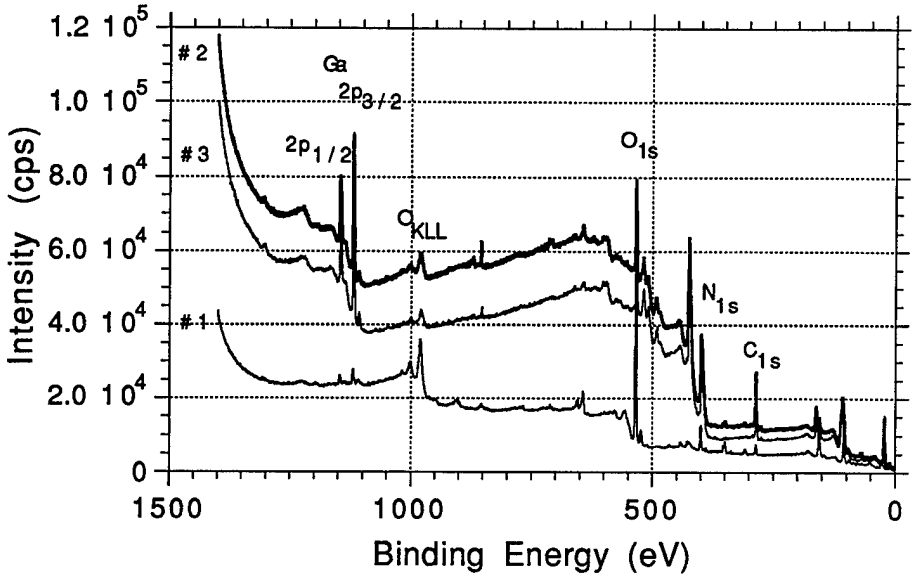



Figure 5. XPS spectra of Sample #1 through #3.

Table I. Growth Conditions for Several Samples

| | Sample #1 | Sample #2 | Sample #3 |
|---|---|---|---|
| TMG bubbler temperature | -19°C | -19°C | -10°C |
| He flow through TMG bubbler | 5 sccm | 10 sccm | 10 sccm |
| He flow bypassed TMG bubbler | 5 sccm | 20 sccm | 30 sccm |
| Stagnation pressure at TMG bubbler | 234 Torr | 530 Torr | 695 Torr |
| Stagnation pressure at TMG nozzle | 212 Torr | 500 Torr | 660 Torr |
| $NH_3$ nozzle temperature | 600°C | 600°C | 600°C |
| $NH_3$ flow rate | 14.5 sccm | 14.5 sccm | 14.5 sccm |
| He flow rate through $NH_3$ nozzle | 100 sccm | 100 sccm | 100 sccm |
| Stagnation pressure at $NH_3$ nozzle | 515 Torr | 515 Torr | 515 Torr |

As the XPS spectra of Sample #2 and Sample #3 are closely similar to that taken from a thick GaN film as reported previously (March 1996), it can be concluded that these films are thicker than the photoelectron escape length (several nanometers). In fact, this is proved by SEM measurements described below.

The RHEED patterns of Sample #2 and Sample #3 were streaky. The streaks diffracted from the GaN films are broader than those streaks from substrate.

*Thickness Measurement of Grown GaN Films.* Figure 6 shows a cross-sectional SEM photograph of Sample #3. The film thickness is estimated to be 20 nm, and gives an average growth rate of 4 nm/hr. It can be also seen that the film consists of many flat faceted islands. The cause of this film discontinuity is due to the low density of initial GaN nuclei on the sapphire surface.

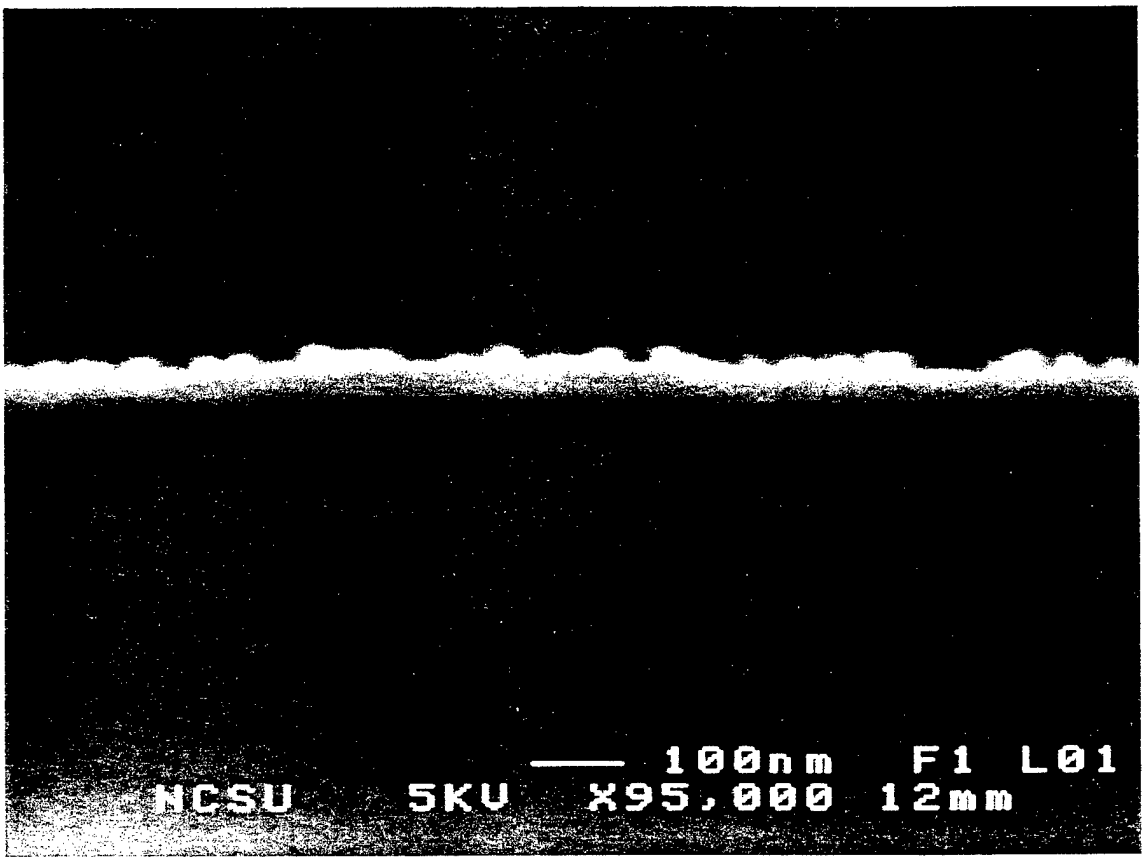



Figure 6. Cross-sectional SEM photograph of Sample #3.

*Ammonia Decomposition.* In order to investigate causes of the low growth rate, mass spectrometry measurements were performed for $NH_3$-seeded beams. As shown in Fig. 7, intensities of $H_2$ and $N_2$ signals increase and intensities of $NH_3$ and $NH_2$ decrease when ammonia nozzle temperature was increased. This indicates that $NH_3$ is decomposing in the nozzle and that the decomposition rate increases with the nozzle temperature.

Figure 8 shows the dependence of $NH_3$ decomposition on the $NH_3$ mole fraction. As can be seen, the decomposition rate increases, passes through a maximum and then decreases as the mole fraction is increased. This suggests that $NH_3$ decomposition was catalyzed by the inner wall of stainless steel nozzle. To solve this problem, nozzles made from titanium will be used in the future.

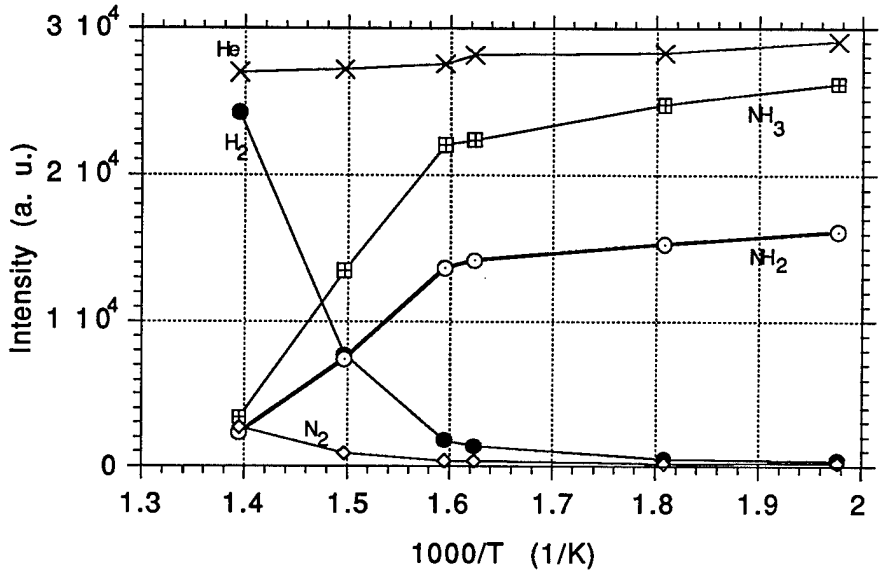



Figure 7. Intensity changes of $NH_3$, $NH_2$, $H_2$, $N_2$ and He species as $NH_3$ nozzle temperature was varied. With the increase of nozzle temperature, $NH_3$ and $NH_2$ intensities decrease while intensities of $H_2$ and $N_2$, which are decomposed from $NH_3$, increase. Note the intensity of He, the carrier gas of $NH_3$ maintains almost at the same level. The flow rates of $NH_3$ and He entering the nozzle were 5 and 100 sccm, respectively.

D. Conclusions

GaN films have been grown successfully by new multi-chamber SEED system. *In situ* RHEED, XPS and SEM results indicate that grown GaN films have reasonable morphology.

E. Future Plans

Optimize system and growth conditions, and grow high-quality GaN films on sapphire and GaN/6H-SiC substrates. Compare properties between heteroepitaxy and homoepitaxy of GaN to de-couple lattice mismatch effect and the effects of supersonic molecular beams.

F. References

1. S. Nakamura, Japan. J. Appl. Phys. **30**, L1705(1991).
2. M. R. Lorenz and B. B. Binkowski, J. Electrochem Soc. **109**, 24 (1962).

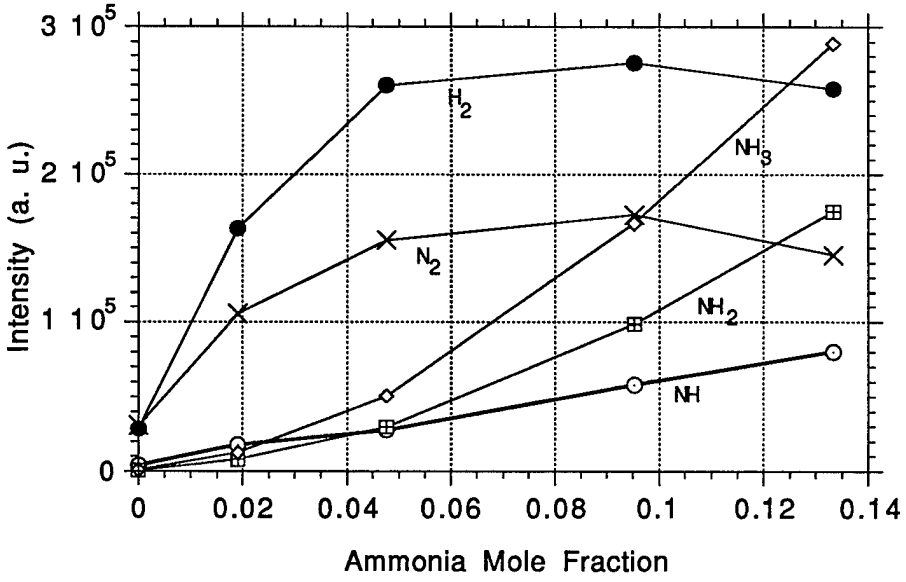



Figure 8. Dependence of $NH_3$ decomposition on $NH_3$ mole fraction which is given by the ratio of $NH_3$ flow rate to the total flow rate (105 sccm) of $NH_3$ and He. The nozzle temperature was 410°C.

## V. Dual Colutron Ion-Beam Deposition

We have successfully completed the alignment of the two Colutron ion-beam systems. However, one of them has developed a vacuum leak and is currently undergoing repairs. The second system can be routinely operated with nitrogen. Mass selected $N_2^+$ and $N^+$ ions with energies at ~20 eV and FWHM ~1 eV can be extracted as shown in Fig. 1(a) and (b), respectively. These essentially monoenergetic and chemically pure ion beams will be used for nitride film deposition in the next few months.

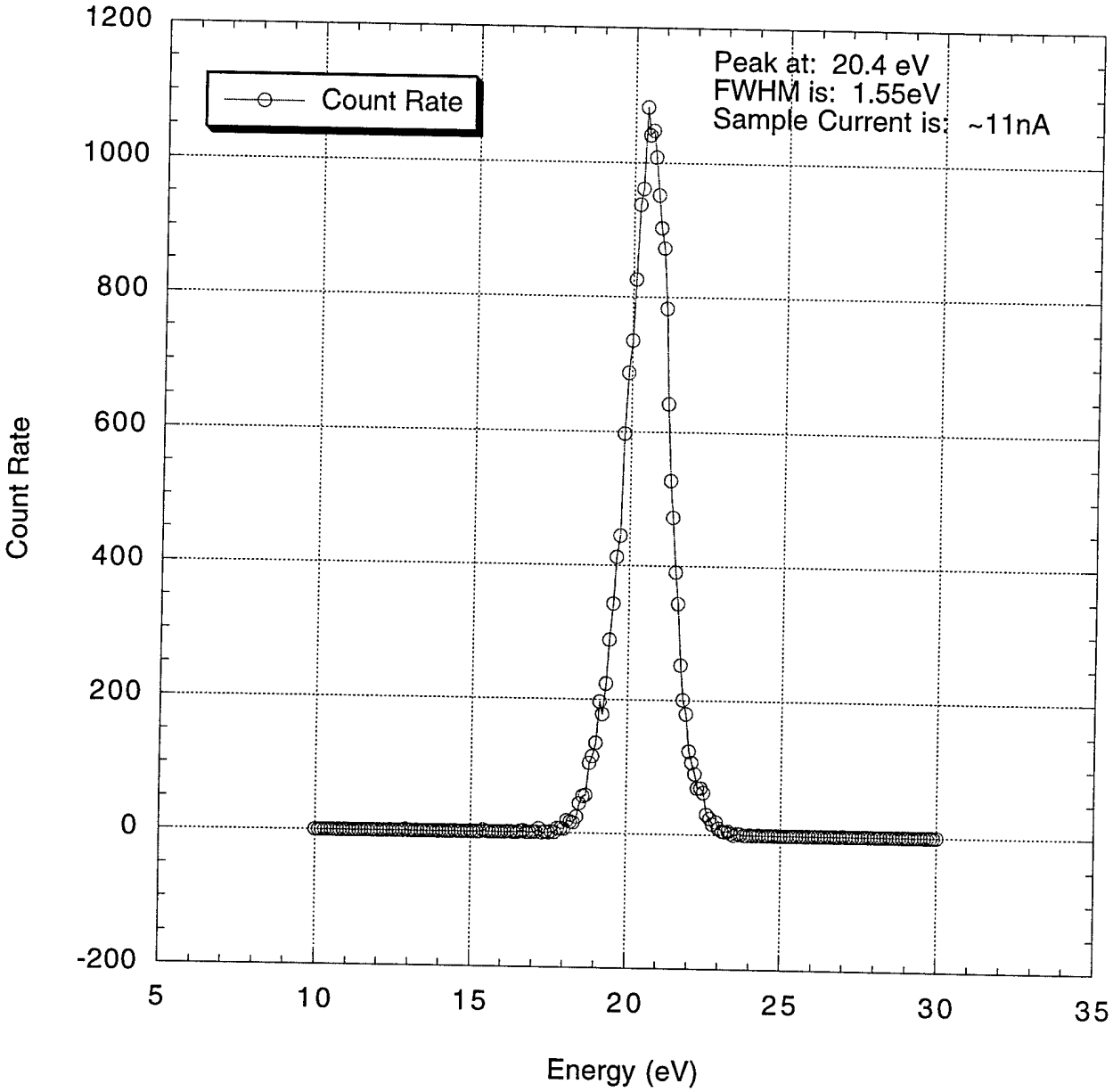



Figure 1(a). Energy distribution of $N_2^+$ ions from the Colutron ion source.

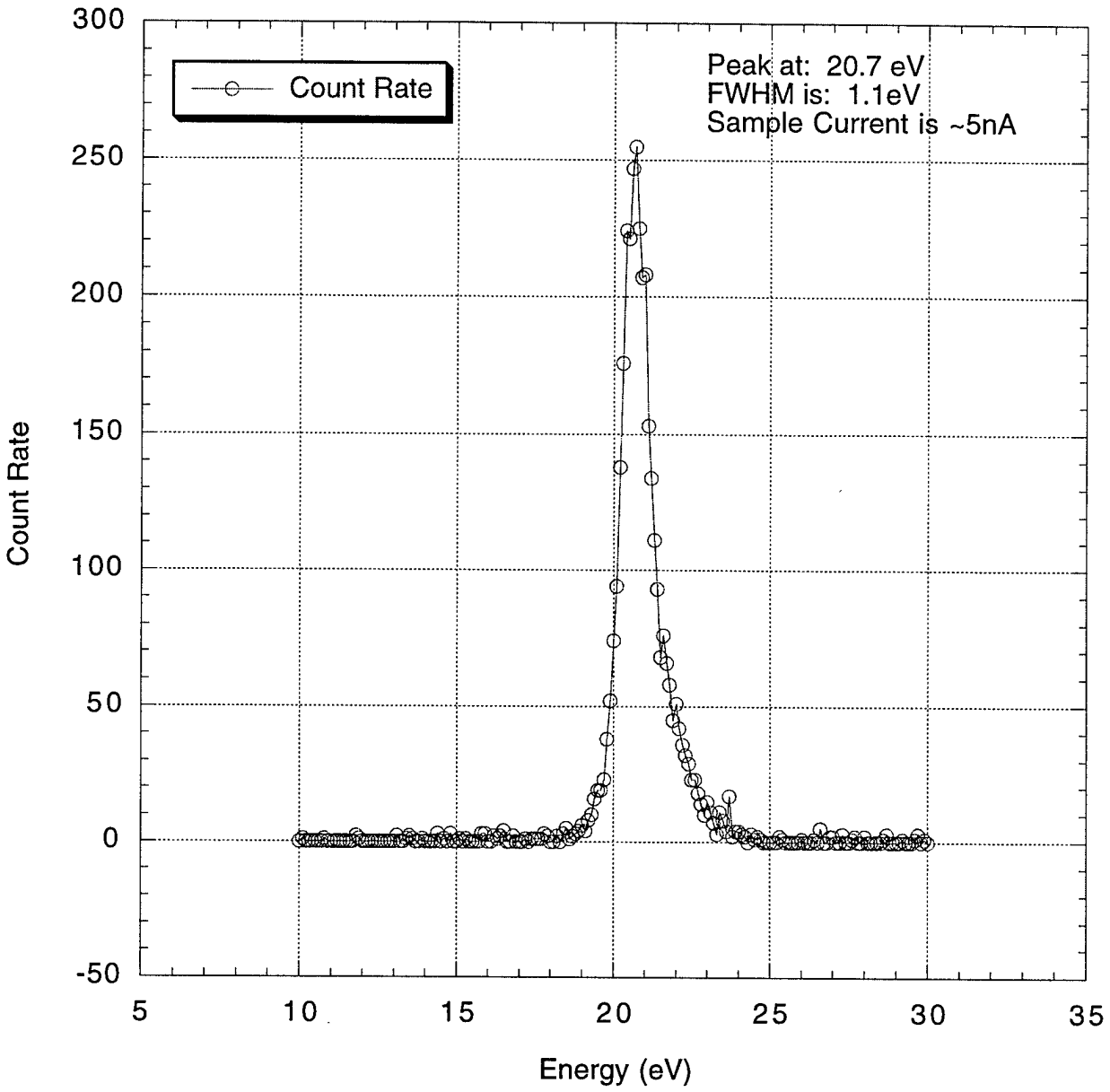



Figure 1(b). Energy distribution of $N^+$ ions from the Colutron ion source.

# VI. Distribution List

| | |
|---|---|
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