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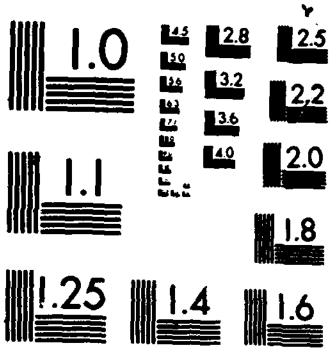

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# Annual Progress Report

# The Growth of Gallium Nitride Films via the Innovative Technique of Atomic Layer Epitaxy

Supported Under Contract #N00014-86-K-0686
for the period June 1, 1986 - May 31, 1987

Robert F. Davis, Calvin H. Carter, Jr.
Michael J. Paisley, and Susan A. Mack
North Carolina State University
Department of Materials Science and Engineering
Campus Box 7907, Raleigh NC 27695-7907
(919) 737-3272 or (919) 737-2347

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This contract involves investigating the efficacy of atomic layer and molecular beam epitaxy techniques for the growth of GaN (a wide direct bandgap semiconductor). During this reporting period the ALE/MBE apparatus was designed, purchased, installed and tested. A neutral atomic nitrogen source was designed and will be ready for construction in mid-July. An interim rf discharge nitrogen source was designed, constructed and used for initial growth experiments. A microwave power supply and resonance cavity have been ordered because recently acquired information indicates this may produce more reactive nitrogen.

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# 1 Introduction

## 1.1 Properties and Applications

Gallium nitride (GaN) is a wide bandgap (3.45 eV at 300K) III-V compound semiconductor. The large direct bandgap and high electron drift velocity of GaN are important properties in the performance of short wavelength optical devices and high power microwave devices. Immediate applications that would be greatly enhanced by the availability of GaN and/or $Al_xGa_{1-x}N$ devices include threat warning systems (based on the ultraviolet {UV} emission from the exhaust plumes of missiles) and radar systems (which require high power microwave generation). Important future applications for devices produced from these materials include blue and ultraviolet semiconductor lasers, blue light emitting diodes (LEDs) and high temperature electronic devices.

Band-to-band transitions in GaN correspond to radiation in the near-ultraviolet region of the spectrum, but by introducing suitable impurities into the material or applying a conventional UV-sensitive phosphor to the finished device (in the case of electroluminescent {EL} applications), it is possible to obtain recombination radiation at various wavelengths throughout the visible spectrum. Extending the laser frequency into the blue regions is very attractive for communications and display applications. Therefore, GaN is potentially useful as a short wavelength semiconductor laser, as an electroluminescent material and as a UV detector. Important applicaions of this last item include UV solar blind detectors and flame sensors for combustion detection and control.

Gallium nitride also possesses two unique properties required in a semiconductor material to be used in fabricating transit-time-limited (IMPATT, etc.) microwave power amplifiers. It is predicted to have a large saturated electron drift velocity[1] which results in short transit times and thus allows the fabrication of high frequency devices. The basis for this prediction comes from a combination of the relatively small effective electron mass in GaN ($m_e = 0.2m_0$), the large optical phonon energy (120 meV) is due to the low mass of nitrogen, and the fact that optical phonon scattering is the primary restriction on the kinetic energy of a hot electron. As a rough approximation, setting $1/2m_e v_s^2 = h\nu_0$, where $v_s$ is the saturated drift velocity and $\nu_0$ is the phonon wave number, one obtains a saturated drift velocity several times greater than either silicon or gallium arsenide.

Also, the bandgap of GaN is more than twice that of GaAs and three times that of Si. Since pair-production thresholds scale with the bandgap, then a GaN transit-time-limited device in reverse bias at high field would be able to operated at higher voltages. This is a result from devices of this type having to be operated at just below the threshold of pair production. In power amplifiers, the power scales as the square of the voltage, thus GaN would have a significant advantage over Si or GaAs.

## 1.2 Limitations

Utilization of GaN has been very limited to date because all material produced to date has possessed an intrinsic n-type carrier concentration of at least $10^{17}$ $cm^{-3}$ and normally more in the range of $10^{18}$–$10^{19}$ $cm^{-3}$. The only high resistivity single crystal material produced has required compensation with a p-type dopant (usually Zn). However, this approach greatly reduces the electron mobility in the film. In addition, intentional growth of p-type GaN has never been acheived, and so devices requiring p-n junctions cannot be produced. (All diode structures produced to date have been metal-insulator-semiconductor {MIS} structures.)

It is a nearly universal consensus that the n-type character is caused by N vacancies produced during the growth process. The basis for this reasoning is that GaN decomposes at $\approx$1123K at a $N_2$ pressure of 1 atm. The vapor pressure of $N_2$ over GaN at 1323K (a common growth temperature used in chemical vapor deposition {CVD} growth of GaN) is 100 atm. Thus molecurlar nitrogen is not used as a source in CVD growth of GaN. A commonly used nitrogen source in CVD growth is ammonia ($NH_3$). The equilibrium vapor pressure of $NH_3$ over GaN at 1323K is only 650 Pa,[2] thus allowing the GaN to form at those elevated temperatures.

## 1.3 Atomic Layer Epitaxy

The authors strongly beleive that substantial improvements in the electronic properties of GaN can be acheived by growing it by the relatively new and innovative technique known as atomic layer epitaxy (ALE) developed in Finland.[3] The principal employment of this process to date has been the production of electroluminescent displays (some reaching 50 cm × 50 cm). A recent and very successful use of this technique has been the growth of CdTe[4] and the more complex solid solution $Cd_xMn_{1-x}Te$.[5] The technique of atomic layer epitaxy has the following advantages:

1. a very high probability of achieving stoichiometry,
2. apparent rejection of impurities,
3. excellent tolerance of substrate temperature and temperature non-uniformity,
4. virtually no control required of the reactant deposition rate,
5. extremely uniform thickness over large areas and precise thickness control,
6. pin hole free films.

The ALE process may be used anytime the binding energy between two different elements in a compound is greater than the binding energies of the reacting elements. This is true in the case of GaN since the binding energy of Ga-N is 364 kJ/mol and those of Ga-Ga and N-N are 138 and 163 kJ/mol, respectively. (The binding energy of diatomic N is 944 kJ/mol, but this type of bond would not be formed at the surface of a growing crystal.) The growth method involves the deposition of a small amount of the cation (or metal) reactant (e.g., Ga) onto a hot substrate followed by a vacuum purge in which all except the first atomic monolayer of this species sublimes. This operation is succeeded by a similar deposition of the anion (or non-metal) reactant (e.g., N) which is also followed by a vacuum purge in which all except one layer of the deposited species sublimes. This sequence is repeated at a cycle time of 2 to 3 seconds with an ensuing growth rate of 1 $\mu$m/h which is equivalent or better than that for the MBE process. Since the adsorption coefficients of impinging atoms by the film depend on the atomic species of the uppermost layer of the film, excess incident atoms that do not form A-B bonds in the film are allowed to re-evaporate (by making use of the larger vapor pressures of the elements than that of the compound) before the next species is allowed to react with the surface. Accordingly, thermodynamic equilibrium of the surface is approached at the end of each step—a situation that is usually not met in other deposition methods. The thickness of the films is determined by the number of elemental deposition layer cycles rather than by the beam intensity and source temperature, as is the case in MBE. Finally, precise control in turning the beams on and off is not essential because each new surface is self-stabilized and is independent of the number of excess incident atoms. Among the materials which have been deposited by ALE to date are ZnS, ZnSe, GaAs, $Al_{1-x}Ga_xAs$, SnTe, GaP, $SnO_2$, $Al_2O_3$, $In_{1-x}Sn_xO_5$, $Ta_2O_5$, CdTe, and $Cd_{1-x}Mn_xTe$. It is by no means limited to these materials.

# 2 Growth and Analysis Equipment

## 2.1 Growth Apparatus

Initially it was expected that the entire atomic layer epitaxy system would need to be designed by our own personnel. However, after extented discussions with many MBE manufacturers* it was determined that a commercial system could be properly modified for ALE growth. Coupled with that was the long time forseen to bring a custom designed system into operational order.

With those factors in mind, negotiations were begun on the purchase of a commercial system modified to provide for ALE-type growth. Discussions were held with these same vendors on the purchase of a system. Finally, Perkin-Elmer was chosen on the

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*Varian Associates, Vacuum Generators, ISA Riber, Perkin-Elmer

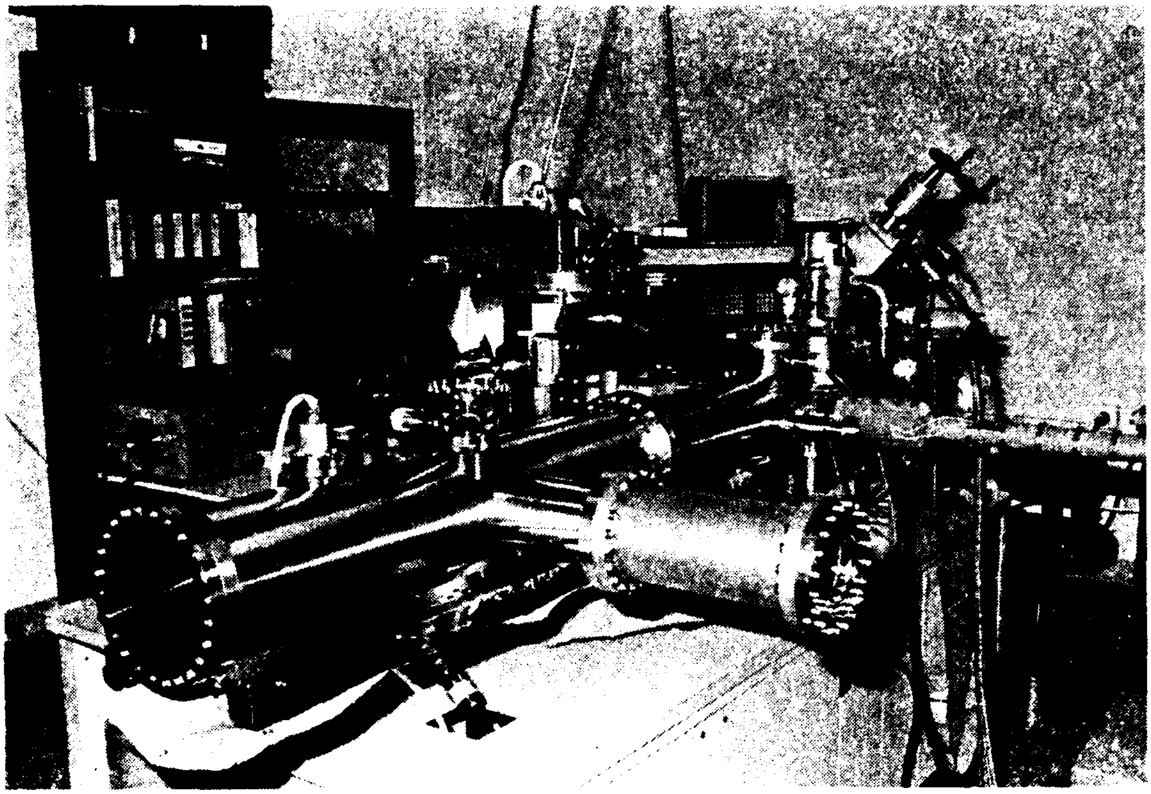

Figure 1: View of entire MBE/ALE system.

basis of sound system design and suitibility for ALE, low cost due to a substantial university donation by P-E, and early delivery (due to another customer not being ready for their system), some 8–10 months before anyone else.

Dr. C. H. Carter and Mr. M. J. Paisley went to the Perkin-Elmer MBE facility in Eden Prarie, Minnesota for a week of MBE training. Many informative discussions were held with MBE personnel concerning system operation as well as overall system design. Additional helpful discussions were held concerning substrate preparation.

The MBE/ALE system[†] was successfully installed into the temporary room in Riddick Labs, though this was not an uneventful period. The entire system is shown in Figure 1. Meeting all of the system specifications required detection and sealing of several leaks including one in the source flange. However, removing the source flange did provide a unique opportunity to see certain construction details. In addition, the replacement of an 8 inch UHV valve was required. After fixing each leak, a bakeout of not less than seven days was necessary to restore the UHV conditions to the chamber. (This proved the extreme utility of the integral quadrapole mass spectrometer.[‡])

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[†] Model 430, Perkin-Elmer Corp., Eden Prarie, MN 55344

[‡] UTI-100C, UTi Instruments Company, Sunnyvale, CA 94086

The growth chamber reached an ultimate pressure of $1.9 \times 10^{-11}$ Torr (specifications were for $5 \times 10^{-11}$ Torr) with liquid nitrogen in the cryopanels. The transfer tube chamber also had very good ultimate pressure of $8.6 \times 10^{-11}$ Torr (specifications were for $1 \times 10^{-10}$ Torr). The reflection high energy diffraction (RHEED) system was demonstrated and all source ovens reached their specified temperature of 1200°C. The parking station heater (located in the transfer tube) and the growth manipulator heater both reached their rated 1000°C.

The MBE/ALE system was equipped with several special features that were necessary for ALE-type growth. An optional cryogenic pumping package[§] along with a variable conductance controller[¶] to provide additional and controllable pumping required by the ALE technique. This pumping package also provided for an additional cryopump[‖] for the load lock which is normally pumped by an ion pump. The cryopump has a much higher pumping speed resulting in reduced loading time. (Note: The variable conductance controller has not yet been installed, it will be installed by the field service engineer as soon as it is available from the manufacturer.) Special carbon element heaters were selected for the parking station heater as well as the growth manipulator heater. These heaters have the capability of >1000°C for silicon dioxide desorption from the silicon carbide substrates. A computer interface module was installed into the multi-loop programmer/controller[**] to extend its capabilities. The controller is normally used to control the source oven temperatures as well as the position (open or closed) of the respective shutters. The interface allows functions of the controller to be monitored and changed from a remote source in a much easier manner. In this case, a microcomputer[††] was chosen to supervise the source controller. This microcopmuter will also be used for accurate shutter control which is critical in ALE-type growth.

After the installation was complete, the gallium and aluminum metal evaporation sources were loaded. The gallium was 99.99999% pure[†] with ≈50 g loaded into a 20 cc pyrolytic boron nitride crucible and the aluminum was 99.9999% pure[‡] with ≈5 g loaded into an identical 20 cc crucible. Both of these sources represent operational problems because they become molten during growth to reach appropriate beam pressures. In the case of gallium, it has a very low melting point (29.7°C) and it expands upon freezing so that crucible breakage is a serious problem. In the case of aluminum, it wets the boron nitride crucible and so it can also cause cru-

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[§] Cryo-Torr 8, CTi Cryogenics, Helix Technology Corporation, Waltham, MA 02254-9171

[¶] UHV Variable Conductance Controller, Kurt J. Lesker Company, Clairton, PA 15025

[‖] Cryo-Torr 100, CTi Cryogenics, Helix Technology Corporation, Waltham, MA 02254-9171. A larger "MC" compressor was part of the package so that the single compressor could operate both pumps.

[**] Model 823 MicRIcon, Research Incorporated, Minneapolis, MN 55424

[††] Apple //e, Apple Computer, Inc., Cupertino, CA 95014

[†] 25 g ingots, Al-Kan Electronic Materials, Scottsdale, AZ 85260

[‡] #00877, Alfa Products, Morton Thiokol, Inc., Danvers, MA 01923

cible breakage upon freezing due to metal penetration into the crucible. For these reasons, these sources are kept molten at all times after the initial melting.

The nitrogen source was also installed on the MBE system at the same time the evaporation sources were loaded. The temporary plasma chamber was removed from the test stand and placed into one of the upper evaporation cell positions on the MBE. An upper cell position was chosen because those cells are close to horizontal thus being less desireable for conventional sources as well as being more convenient to attach the plasma source.

## 2.2 Analytical Chamber

After discussions with the principals involved in the plasma enhanced CVD growth of diamond films (also funded by ONR), it was decided that a combined analytical system would serve both projects more efficiently than separate dedicated systems. It was also decided that a separate analytical chamber would house the analysis equipment in a more efficient manner and still allow the UHV interchange of specimens between the two growth systems and the analytical chamber.

A number of analytical equipment vendors were contacted concerning analytical equipment with primary emphasis on surface oriented techniques. Surface techniques were chosen for primary emphasis because substrate surface conditions are very important in both projects prior to growth as well as subsequent film evaluation. Additionally, bulk analytical techniques are already available elsewhere on campus, and also are not sensitive to exposure to atmosphere.

The analytical chamber will initially make use of reverse view low energy electron diffraction (RVLEED) and X-ray photoelectron spectroscopy (XPS). An electron source will be purchased from next year's funds to allow Auger electron spectroscopy (AES) as well as electron energy loss spectroscopy (EELS). The analysis chamber will also have the flexibility to allow the addition of a scanning-tunnelling microscope (STM). Installation and use of the STM would be dependent upon receipt of additional funding.

Discussions were held with Dr. Gar Hoflund of the University of Florida to aid in the design of the analytical systems. His extensive background in analytical techniques and UHV design has already been very helpful. At his suggestion, a slit will be added to the front of the electron analyzer to permit angle resolved AES and XPS. Furthermore, ports were added to the design to permit the addition of the following techniques: ultraviolet photoelectron spectroscopy (UPS), secondary ion mass spectroscopy (SIMS), ion scattering spectroscopy (ISS), electron stimulated desorption (ESD), and inverse photoelectron spectroscopy (IPS).

The RVLEED[§], electron energy analyzer[¶], and x-ray source[‖] have been delivered. The analysis chamber is currently in the final design stage and will be submitted for bids to various chamber manufacturers in July. A schematic drawing of the current design for the analytical chamber is shown in Figure 2.

# 3 Nitrogen Source

## 3.1 Plasma Source

The neutral atomic nitrogen source will not be ready for some time (with perhaps the procurement of additional funds). Thus with the MBE/ALE system in place an interim nitrogen source was needed. Use of nitrogen gas alone was not expected to result in good GaN films given the strength of the N-N bond (9.84 eV).[6] Thermal cracking of ammonia was also not chosen because of the high temperatures required and uncertainty of the deleterious effects of the hydrogen on the growing films.[7] Discussions held with Dr. Orlando Auciello in the nuclear engineering department at NCSU resulted in the current design for a glow discharge plasma-activated nitrogen source. A sketch of the plasma source is shown in Figure 3.

The nitrogen is supplied from a compressed gas bottle regulated to ≈5 psig and pass through a nitrogen gas purifier.[†] After being purifed by the hot (600°C) copper charge the nitrogen gas passes through a UHV compatible leak valve[‡] to control the gas flow into the plasma chamber. Next the gas passes through a metal-glass seal and then a small orifice designed to keep the plasma from traveling up the gas stream to the leak valve where it could pick up some potential contamination. Once in the plasma chamber it is excited by a small rf generator[§] operating at 13.56 MHz at a rated maximum power of 300 W. Once atomized the nitrogen passes through the exit orifice. This orifice is designed to be removable and so it is mounted in a "greaseless" glass joint.[¶] (Changing the orifice requires demounting the wax seal in the outer chamber.) The choice of a plasma chamber made entirely of glass was made based on the low recombination coefficient of glass.[6] The changable orifice is necessary to optimize the resulting beam flux versus the plasma chamber pressure which cannot be measured directly due to the presence of the plasma. Once it is optimized, a second chamber will be built without the demountable seals and will

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[§] RVL-8, Princeton Research Instruments, Inc., Princeton, NJ 08542

[¶] MAC-2, Instruments SA, Riber Division, Metuchen, NJ 088440

[‖] Instruments SA, Riber Division, Metuchen, NJ 088440

[†] Model 2B-20-Q, Centorr Associates, Inc., Suncook, NH 03275

[‡] Series 203 Variable Leak, Granville-Phillips Co., Boulder, CO 80303-1398

[§] Model HF-300, ENI Power Systems, Inc., Rochester, NY 14623

[¶] ST 14/20 clear-seal, Wheaton Scientific, Millville, NJ 08332

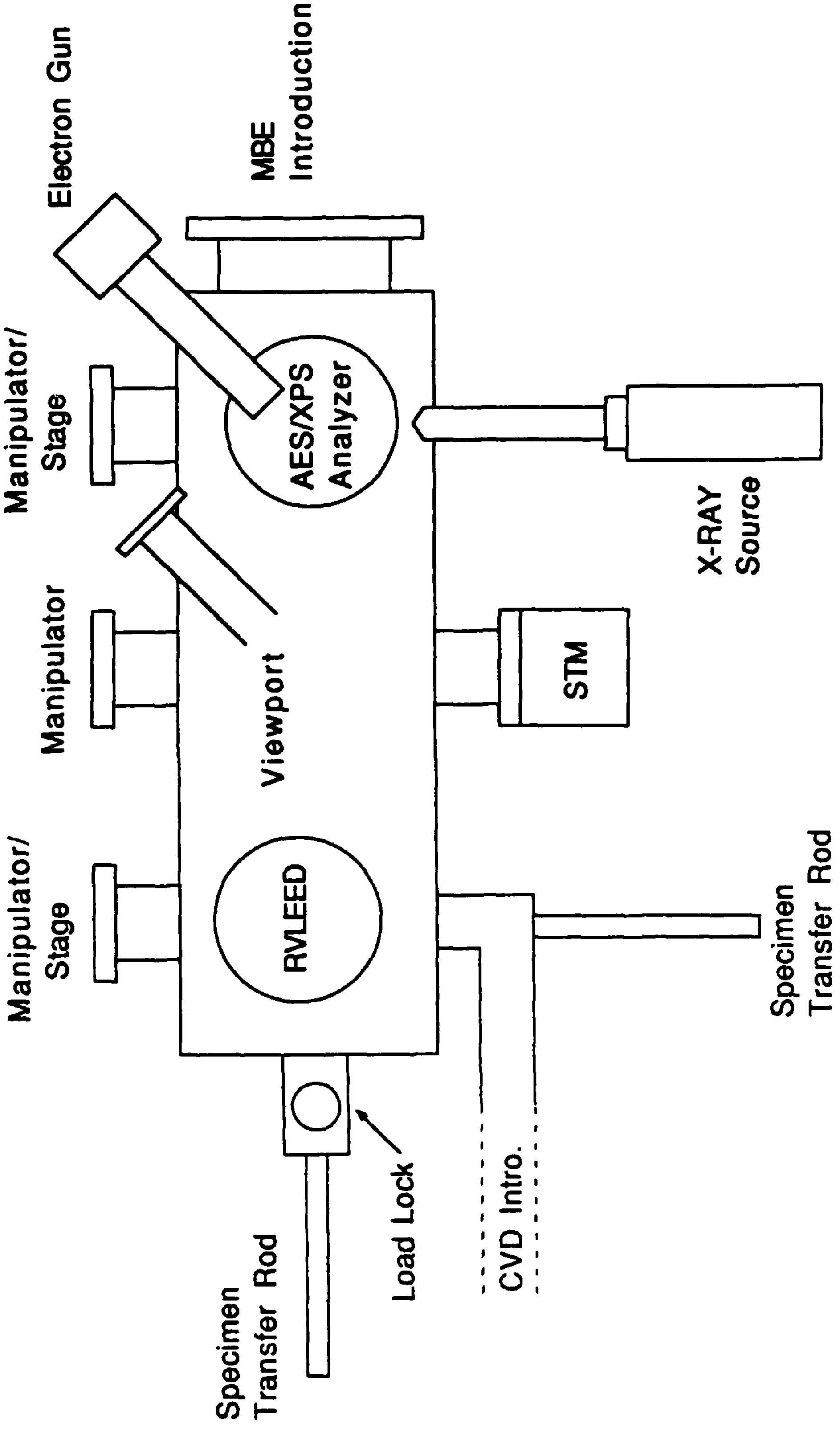

Figure 2: Schematic of the analysis chamber.

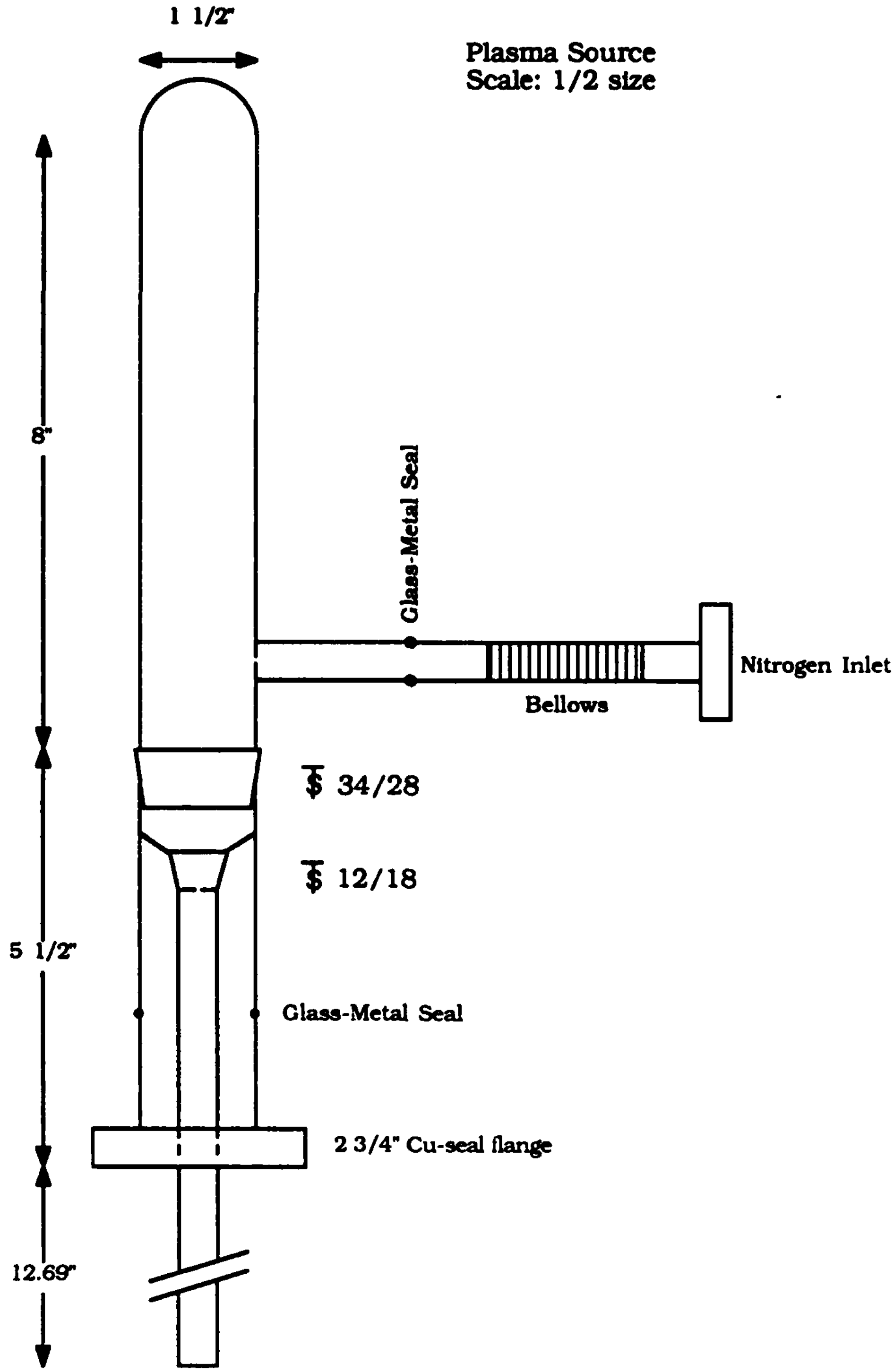

Figure 3: Sketch of the interim glow discharge plasma source for nitrogen.

thus be more UHV compatible.

Choice of the aperature diameter required to contain the plasma is based on the same equation for the thickness of the boundary layer along the chamber walls where no plasma exists.[8] Note that the chamber radius (assuming typical cylindrical geometry) must be greater than this value or there will be no plasma in the chamber. This boundary layer thickness is given by the Debye length[9] as:

$$\lambda_D = \sqrt{\frac{\varepsilon_0 k_B T_e}{ne^2}}$$

where $\lambda_D$= Debye length, $\varepsilon_0$= permittivity of free space, $k_B$= Boltzmann's constant, $T_e$= electron temperature, $n$= electron density, and $e$= electronic charge. If the radius of an opening exists which is greater than the Debye length, then the plasma will not remain confined.[6]

The long tube after the exit aperature is designed to contain and help collimate the nitrogen beam. The end of the source will terminate as the other sources do, just before the tantalum shutter. The rf generator was located on a small table with the leak valve and gas purifier along with a shielded capacitor used to match the power generator to the load of the nitrogen glow discharge plama. This is shown in Figure 4.

## 3.2 Atomic Nitrogen Source

Very low energy, neutral, atomic nitrogen is an ideal source of nitrogen for MBE/ALE of gallium nitride. Atomic nitrogen is orders of magnitude more reactive than other sources of nitrogen such as $N_2$ or ammonia, reacts without requiring bond breaking or steric rearrangement, and produces no reaction by-products. Low energy, on the order of the band gap, prevents implantation and sputter damage of the deposited film, both highly deleterious to the ALE process. Neutralization will eliminate difficulties associated with charging, particularly non-uniform growth or unstable deposition processes.

The nitrogen source will consist of a plasma ion source, mass separator, and appropriate ion optics. The ion beam is neutralized at the substrate by a hot filament electron source installed in a separate port. The apparatus includes a gate valve, differential pumping, and beam blanking plates. The source is in the final design stage and should be ready for fabrication by mid-July. Figure 5 is a schematic of the current design. Before the source is used with the MBE system it will be operated on a test stand designed and built expressly for this purpose.

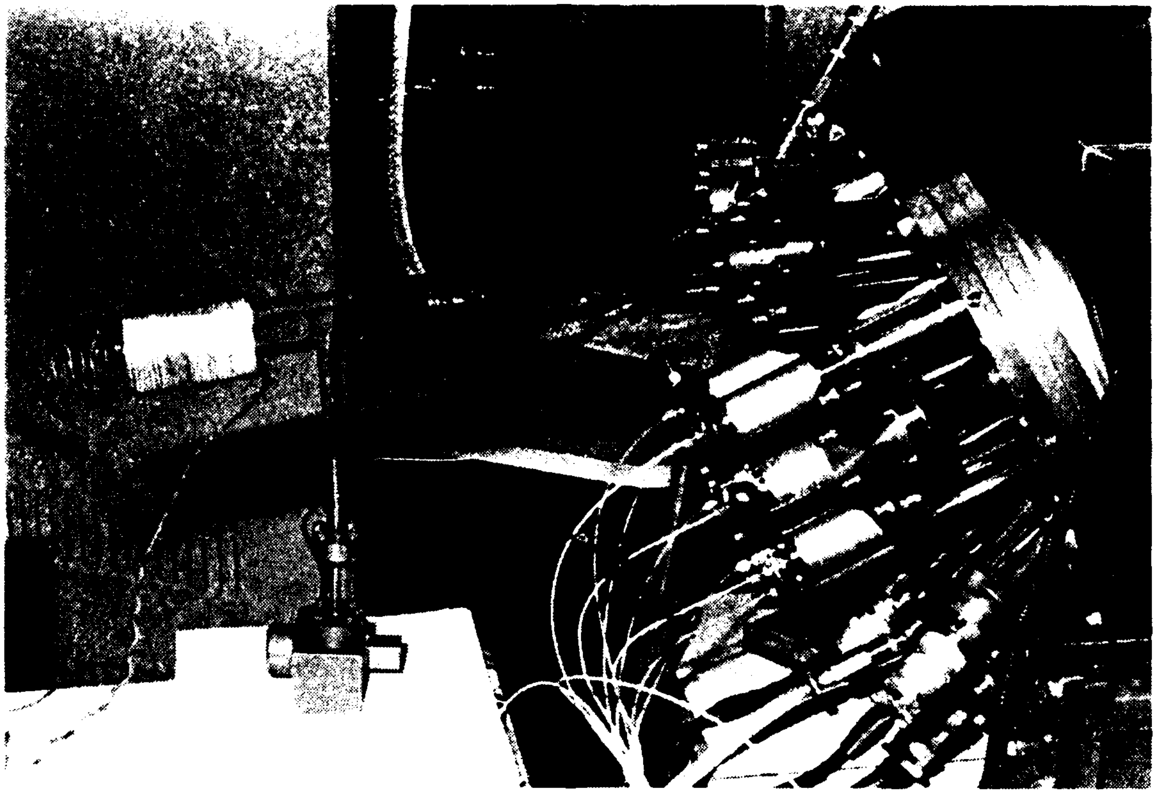

Figure 4: Layout of the glow discharge plasma chamber as attached to the MBE/ALE growth chamber.

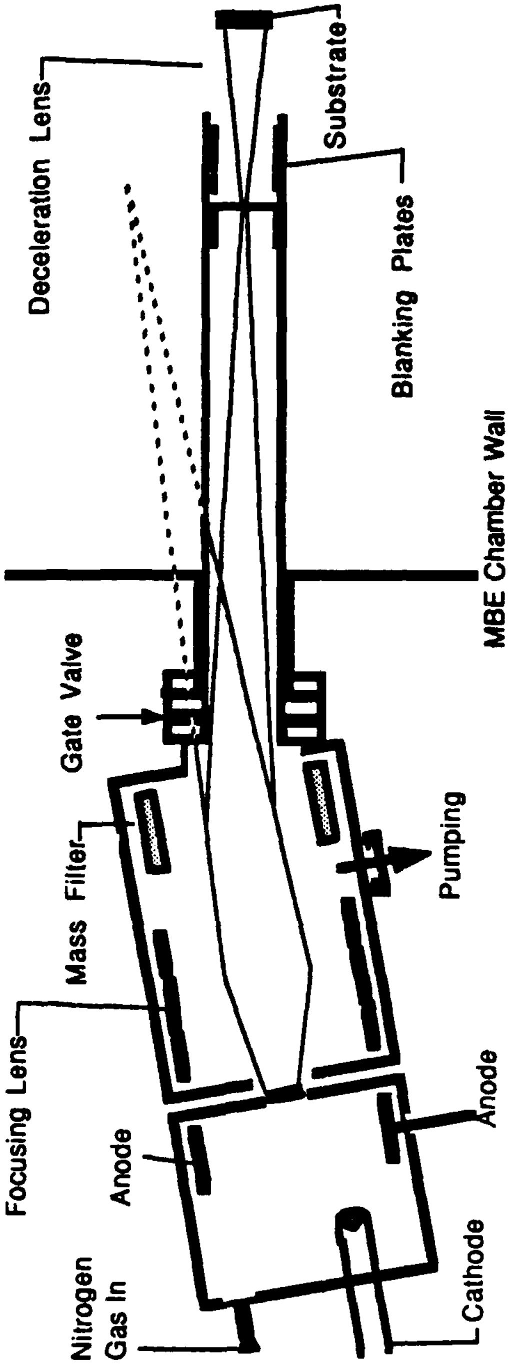

Figure 5: Schematic of the atomic nitrogen source.

### 3.2.1 Ion Source

The ion source is perhaps the most critical aspect of the nitrogen source. Both a Kaufman ion engine and a Colutron ion source were evaluated. Although the Kaufman-type source has high divergence and energy spread compared to the Colutron, it also has far more ion flux. Controlling the divergence and energy spread should be less difficult than compensating for inadequate flu so the Kaufman source will be used.

In order for ions to impinge upon a substrate with a specific energy, 5 eV in this case, the difference between the potential at which the ions are created (i.e., inside the ion source) and the substrate potential must be equal to that energy. This is true regardless of the number, potential, and configuration of the intervening ion optical elements. Consequently, if the substrate is to be held at ground, as is usual for MBE deposition, the ions must be created at 5 eV. Alternately, the ions may be created at a higher energy, but this requires that the substrate be biased.

The former approach was investigated first, due to the difficulties inherent in biasing the MBE substrate. It is theoretically possible to create and extract 5 eV ions with the Kaufman source, but the resulting ion flux is low, and divergence is high. The second approach, that of using higher energy ions and a biased substrate, is currently being investigated. The Kaufman source has high flux and acceptable divergence when ions are created at 1500 eV.

### 3.2.2 Optics

After the ions are created they must be extracted from the source and directed toward the substrate with minimum ion loss. Extraction is achieved with a pair of grids at the opening of the source. A recent development in ion source optics is the use of curved grids to reduce the divergence of the emerging ion beam. Although this type of grid system is difficult and more expensive to fabricate, the reduction in ion losses associated with the use of dished grids offsets the expense.

Ion lenses are used to control the beam after extraction. In general minimizing the number of times the beam is brought to crossover also minimizes ion losses. The current design has only one crossover, necessary for the beam to pass through a differential pumping aperture. This crossover is achieved by an Einzel lens placed near the Kaufman source. The beam is focused and drifts in field free space through the mass separator and finally through the differential pumping aperture. The aperture acts to decelerate the beam as it travels toward the substrate. A final lens is placed after the aperture to control the beam divergence caused by deceleration and space charge.

Computer modelling of the ion optics has been an invaluable tool. SIMION,[†] the modelling program, computes and graphically displays the field lines and ion trajectories corresponding to lens data input by the operator. The computerized trial and error eliminates the need for lengthy, complicated longhand calculations and sharply reduces the amount of trial and error necessary to build a working source.

### 3.2.3 Mass Separation

Mass separation will be achieved using an E×B or Wein velocity filter. This type of mass separator uses electric and magnetic fields perpendicular both to each other and to the beam; these fields exert opposing deflection forces upon charged particles moving through the filter. For a particle with velocity $v = E/B$ the opposing forces balance and the particle passes through the filter undeflected, while particles with other velocities are deflected away from the path at specific angles depending upon velocity. Deflected particles are intercepted with a mass separation aperture. Since all particles in the beam to be separated have the same energy, their velocities vary inversely with the square root of the particle mass; thus the E×B velocity filter acts as a mass separator so long as the energy spread of the beam is low.

Normally the undeflected portion of the mass separated beam is "accepted" while the deflected portions are intercepted with a mass separation aperture. In this design, however, the mass filter will be set such that particles of mass 16 are undeflected (i.e., $CH_4^+$, an expected beam contaminant) while the $N_1^+$ is deflected at some (known) angle; the source will be bent at the same angle so the separated $N_1^+$ beam passes through the aperture. The result is simultaneous mass separation of unwanted charged particles and elimination of neutrals, which are unaffected by ion lenses and the mass filter. The mass separation aperture will also be used as the differential pumping aperture and will form the end of the drift tube.

### 3.2.4 Neutralization

The original approach was to neutralize the beam by charge exchange before it left the source, either by passing the beam through a gas filled charge exchange cell or by grazing incidence on a solid plate. Great problems are inherent in both methods; the gas cell is inefficient and adds a large gas load to the MBE system, while the solid plate is difficult to implement and is expected to introduce uncontrollable divergence of the beam. Once beam ions are neutralized they can no longer be controlled with

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[†] SIMION 2.0, D. A. Dahl and J. E. Delmore, Idaho National Engineering Laboratories, Idaho Falls, Idaho 83415. SIMION runs on a IBM PC with 640K RAM, an EGA display adapter, the math coprocessor, a mouse, and the IBM Graphics Toolkit. It is run at NCSU on an IBM AT (8 MHz clock), with the 80387 math coprocessor, and a 30 MB hard disk.

ion optics, so any divergence or irregularity introduced by neutralization cannot be corrected.

It appears that a better approach is to build a source of low energy nitrogen ions, then balance the charge at the substrate with a hot filament electron source installed in a separate source port. This achieves the original intent of limiting charge buildup at the substrate while eliminating difficulties involved with gas cell or solid plate neutralization. The electrons will have very little acceleration energy to prevent electronic damage to the film. The current source design will implement this latter approach.

### 3.2.5 Other Features

The ion source will have several other features as well. Since the Kaufman source operates at a pressure of $\approx 7 \times 10^{-5}$ Torr while the MBE should have a background of $10^{-9}$ Torr or better, the nitrogen source will be differentially pumped. The pumps already in use on the test chamber are expected to be adequate for this purpose. A gate valve will be interposed between the E×B filter and the MBE system so filament changes can easily be made on the Kaufman ion engine. Finally, blanking plates will be incorporated to act as a very fast beam shutter.

### 3.2.6 Remaining Challenges

Several challenges remain in the development of the atomic nitrogen source. First, biasing the substrate is non-trivial, but possible. We are currently discussing methods of biasing the substrate with the design people at Perkin-Elmer. Second, the substrate is tilted with respect to the axis of the source port, which may necessitate a final lens at the substrate or some other method of deflecting the beam so most of the ion trajectories are normal to the substrate surface. Further, the final calculations must be made and the lenses modelled with the SIMION computer model.

## 4 Initial Growth Results

Initial growth of GaN films was done using conventional MBE techniques since the variable conductance controller necessary for the ALE technique was not yet installed. The MBE/ALE system was used for growth runs beginning only two weeks prior to this report. Initial growth runs did little more than establish inital parameters for gallium and nitrogen flux conditions, substrate preparation, and proper RHEED conditions.

## 4.1 Substrate Preparation

Initial growth studies were conducted on (100)-oriented $\beta$-SiC substrates. (This material has the cubic zinc blende structure.) The $\beta$-SiC films were epitaxially grown on (100) Si substrates by CVD of Si and C from pyrolysis of highest purity $SiH_4$ and $C_2H_4$ entrained in $H_2$, in an rf-heated cold-wall barrel-type reactor designed and constructed in house especailly for this purpose. The growth temperature was 1360°C and growth rates were typically 2 $\mu$m/h. The films were deposited for 2–3 h so that the SiC film upon which the GaN was grown was $\approx$4–6 $\mu$m. The substrates were subsequently polished with 0.1 $\mu$m diamond paste and then oxidized at 1200°C in flowing dry oxygen for 1.5 h to consume the 50 nm of surface which contains polish damage.

Just prior to mounting the substrate on the MBE sample block, the substrates were etched in 49% HF for 60 s to remove the grown oxide from the surface. The substrates were then transported in fresh de-ionized water to be mounted on the MBE sample blocks. The block (made of molybdenum) has a groove around the circumference of the block to permit movement of the block throughout the MBE/ALE system via a fork-style transporter. There are also a number of small holes around the circumference to allow a small diameter wire to be applied to act as a film thickness mask.

The substrate block is placed on a standard laboratory hot plate[‡] and heated to above the melting point of indium ($\approx$150°C). A small amount of indium [§] is placed on the block and spread into a flat molten film using a molybdenum foil held in a pair of wide-tip forceps. Then the substrate is placed on the block and moved around in the indium until there is good contact between the indium and the substrate. This step is important in holding the substrate in place on the block as well as obtaining uniform heat transfer to minimize temperature non-uniformity during film growth. The block is then removed from the hot plate and allowed to cool. It is then loaded into the substrate block carrier and loaded into the MBE/ALE system load lock.

The load lock is heated to $\approx$50°C for initial outgassing of the substrate cassette. The low temperature limit is due to the polymeric O-ring seal. The load lock is initially evacuated by the system's three sorption pumps and has its own small cryopump for acheiving near-UHV conditions. The cryopump will pump the load lock to the $\approx 1 \times 10^{-8}$ Torr range, though moving the cassette into the transfer chamber can

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[‡] Model 200T, Fisher Scientific Company, Pittsburgh, PA 15219

[§] #00154, Alfa Products, Morton Thiokol, Inc., Danvers, MA 01923 occur as high as $1 \times 10^{-6}$ Torr, and typically occurs in the low $10^{-7}$ Torr range. Once in the transfer tube which easily reaches $<3 \times 10^{-10}$ Torr, substrates can be freely moved about for outgassing, oxide removal, and thin film growth.

## 4.2 Growth Conditions

Once in the transfer tube the films require the removal of a thin layer of $SiO_2$ formed by exposure to the atmosphere during mounting on the substrate block. This is accomplished by heating the substrate to a high temperature in the UHV conditions of the transfer tube and allow the oxide to desorb from the surface of the film. Initial desorptions have been done at temperatures of 800–850°C. The very first desorption was done at 1050°C which resulted in large amounts of indium evaporating from the substrate block. The resulting RHEED patterns indicated a very thin oxide remained since the diffraction pattern was quite visible but the individual spots were still diffuse. Additional work will be required to develop a good oxide desorption procedure.

After the desorption procedure, the substrate is loaded into the growth chamber. While the sample is cooling down to the 300°C limit for transfer, the Ga source is ramped to growth temperature and the chamber cryopanels are cooled down with liquid nitrogen. (The source flange is an exception since is was modifed to allow water cooling, since its liquid movement passages do not permit very effective heat transfer with liquid nitrogen.) The source beam fluxes are then measured with the integral quadrapole mass spectrometer. Initial growths were done at Ga pressures of $2 \times 10^{-8}$ Torr–$5 \times 10^{-7}$ Torr and a nitrogen pressure of $5 \times 10^{-6}$ Torr. The nitrogen was activated with the inductively coupled rf generater at adsorbed power levels of 10–40 W. The sample is then placed on the growth manipulator and set to a rotation speed of $\approx$10-15 rpm. The nitrogen source is operated (i.e., shutter open) while the sample is heated to the growth temperature of 700°C. Once the sample temperature has stabilized, the Ga shutter is opened and growth begins. Growth runs last two hours to provide a measurable film thickness. At the end of the growth period, the Ga shutter is closed and the source is cooled down. Then the sample is cooled down after which the nitrogen source is shut down and the liquid nitrogen is turned off. At this point, the sample is ready for removal or RHEED examination.

## 4.3 Film Evaluation

After the samples were removed from the system, they were examined with an optical microscope to a magnification of 1100X. Next, the samples were polished with 0.1 $\mu$m diamond at an angle of 0° 34′. This angle provides a linear magnification of 100X of the thickness of the film. Unfortunately, the initial growths showed no apparent film of GaN (minimum thickness resolution ≈100Å). There was evidence of free Ga droplets on the film surface.

# 5 Future Work

## 5.1 Substrates

Silicon carbide was chosen as the substrate for growing GaN because its lattice parameter and coefficient of thermal expansion are muich closer to those of GaN than is sapphire (the most common substrate used in pervious growth studies of GaN). The (100) plane of $\beta$-SiC is not the best lattice match to GaN but it was chosen because films with this orientation were immediately available.

However, (0001) $\alpha$-SiC is a very good choice because it has a wurtzite structure (the same as GaN) with lattice parameters of $a$= 3.0806 Å and $c$= 15.1173 Å, compared with $a$= 3.189 Å and $c$= 5.185 Å for GaN. Since it has the same structure and similar lattice paramters ($\Delta a$= 3.4%), it makes a good choice for a substrate material. $\alpha$-SiC has the additional advantage of having a thermal expansion coefficient different from GaN by 16% as opposed to 25% for sapphire. The growth of $\alpha$-SiC crystals in our laboratories has recently reached the point that they are suitable (and available) for use as substrates and will be used during the next reporting period.

Finally, the ALE/MBE system is capable (by using the aluminum evaporation source) of growing $Al_xGa_{1-x}N$ buffer layers where the Al/Ga ratio is varied from that of AlN to GaN. This will allow growth to begin as AlN ($a$= 3.111 Å) and then be slowly graded into GaN.[10,11] Of course, this will also allow the growth of compositionally complex layered structures such as superlattices.

Alternative substrate oxide desorption procedures will be tried. Most notable among these are the use of group III elements to decompose and evaporate the oxide. The procedure is to expose the substrate to the elemental beam (either Ga[12] or In[13]) at a sufficiently high temperautre to permit the resulting oxides to evaporate.

## 5.2 Nitrogen Source

Eventually, the nitrogen source discussed in Section 3.2 will be the source used for growth of GaN. As mentioned in Section 3.1, an interim plasma source is being used. It is planned to modify this source in several ways to increase its effectiveness during growth.

Several modifications will be made to increase the effectiveness of the disassociation of the nitrogen. A capacitor network is being built by the electronics shop at NCSU to permit better impedance matching between the plasma source and the rf generator which will allow more power to be applied to the nitrogen gas. Mixtures of He and $N_2$ will be used since the helium will induce Penning ionization[6] (and disassociation) in the nitrogen. (Argon may be attempted as well, since it pumps much more easily than He, though its excited state is only sufficiently energetic to cause disassociation and not Penning ionization.)

A different source of power will be tried for the nitrogen plasma. Microwave frequencies have higher energy electron distribution functions[14] and thus are much more efficient at creating atomic nitrogen compared with rf frequencies. A microwave source may acheive 90% production of atomic nitrogen.[15] A microwave power supply[¶] and waveguide[‖] have been ordered as well as necessary hardware to build a second glass plasma chamber.

## 6 Facilities

The current temporary facility in Riddick Laboratories has been quite adequate for the system in its initial stages of operation. However there is not enough space to add both the analytical chamber described in Section 2.2 and the attached RPCVD system which shares the analytical chamber. Therefore, the MBE system and its support equipment will be moved to the new NCSU Research Facility on the University's newly planned Centennial Campus. Work has been progressing steadily on the construction of this new building. At the time of this writing, half of the foundation for the building has been completed and initial occupancy is expected on October 15, 1987. This new laboratory facility will be well equipped with a modern Class 100,000 environment, controlled systems for storage and use of hazardous gases, and complete utilites including piped in liquid nitrogen. A sketch of the proposed laboratory layout is shown in Figure 6.

Note the load lock areas to maintain the clean room environment. This is further maintained by all services being routed external to the laboratories in a rear corridor not shown. Inside the laboratories located at the equipments's load lock will be a localized area of Class 100 conditions for substrate preparation and loading. Thus prior to growth, the substrate will be exposed to only very clean conditions.

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[¶] MPG-4M, Opthos Instruments, Inc., Rockville, MD 20855

[‖] Evenson cavity, Opthos Instruments, Inc., Rockville, MD 20855

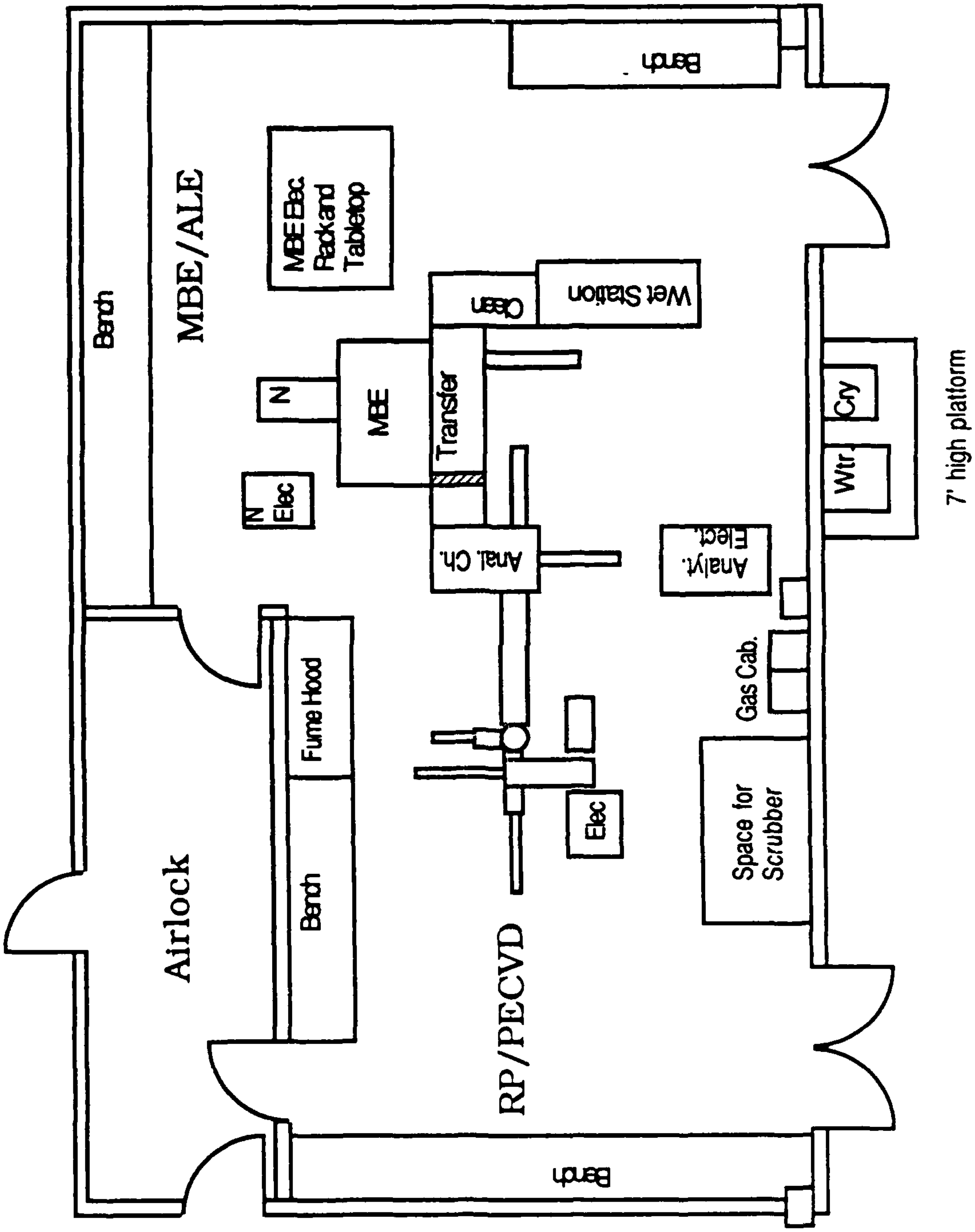

Figure 6: Sketch of the laboratory layout for the MBE ALE facility.

## 7 Related Activities

Three activities of interest were undertaken during the past year. First, R. F. Davis, C. H. Carter, and M. J. Paisley attended a workshop presented by the North Carolina Section of the Materials Research Society entitled "Plasma-Surface Interaction and Processing of Materials." During this workshop one session was chaired by R. F. Davis. Second, C. H. Carter, Jr., attended a workshop entitled "Process Plasma Diagnostics" held by Princeton Scientific Consultants. Several related ideas on both nitrogen plasma generation and characterization resulted from information obtained at this workshop. The final activity of note was the submission of an abstract for a paper to be presented at the fall meeting of the American Vacuum Society in Anaheim, California. The details of the conference along with a copy of the abstract submitted is included below.

Society: American Vacuum Society
Meeting: 34th Annual Symposium & Topical Conference
Dates: November 2–5, 1987
Location: Anaheim, California
Session: JS-6: Novel Semiconductor Materials and Heterostructures
Title: Growth of Gallium Nitride Thin Films via Modified MBE Techniques
Published: Will be published in proceedings issue of the Journal of Vacuum Science and Technology A in May, 1988.
Abstract: Gallium Nitride is a compound semiconductor with a direct, wide bandgap (3.5 eV at 300K) and a large saturated electron drift velocity. This unique combination of properties provides the potential for fabrication of short wavelength (near UV and blue) semiconductor lasers, LEDs and detectors as well as transit-time-limited (IMPATT, etc.) microwave power amplifiers from this material. However, all GaN previously produced has possessed a high n-type carrier concentration which has limited its potential. This phenomenon has been almost invariably assocated with the presence of nonequilibrium nitrogen vacancies. This paper reports growth of GaN by modified MBE techniques in order to reduce the nitrogen vacancies. The primary advantages of these MBE-based techniques are low growth temperature and high nitrogen activity. A standard effusion cell is used for the gallium source, but for nitrogen, a RF glow discharge is used to activate the nitrogen prior to deposition. Both simultaneous and sequential (i.e., atomic layer epitaxy) deposition of source species were employed to evaluate the impact on film quality. The films were deposited on both (100) $\beta$-SiC and (0001) $\alpha$-SiC substrates. Growth results and preliminary film characterization will be presented.

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