**AD-A204 359**

**TITLE:** Deposition of Device Quality Epitaxial Layers of Gallium Nitride for Electronic Applications

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**DATE:** February, 1989

**ABSTRACT:**

See Title Page

**DISTRIBUTION/AVAILABILITY:** Approved for public release; distribution unlimited

**REPORT SECURITY CLASSIFICATION:** Unclassified

**RESTRICTIVE MARKINGS:** None

**MONITORING ORGANIZATION:** Office of Naval Research

**ADDRESS:** 800 Quincy St., Arlington, VA 22217

**NAME OF FUNDING/SPONSORING ORGANIZATION:** Office of Naval Research

**ADDRESS:** 800 Quincy St., Arlington, VA 22217

**PROGRAM ELEMENT NO.:** 61153N

**PROJECT NO.:** 4145

**TASK NO.:** 210

**PROJECT/ACCCESSION NO.:** 01

**SOURCE OF FUNDING NUMBERS:**

<table>
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<th>PROGRAM ELEMENT NO.</th>
<th>PROJECT NO.</th>
<th>TASK NO.</th>
<th>WORK UNIT</th>
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**SUPPLEMENTARY NOTATION:**

See Title Page

**ABSTRACT SECURITY CLASSIFICATION:** Unclassified

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**OFFICE SYMBOL:** J
Gas Source Molecular Beam Epitaxy Deposition
of Device Quality Gallium Nitride

Office of Naval Research Grant N00014-84-K-0274

February 1989

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Abstract

Deposition of the first layers of gallium nitride will occur by the end of February. We have spent the last six months assembling our experimental equipment which includes selecting and ordering a plasma activated nitrogen source, building a nitrogen delivery system and bringing up our gas source MBE. A brief report of our research goals for GaN is given.
INTRODUCTION

GaN is a III-V semiconductor of enormous potential for device applications. It combines a wide direct band gap (3.4 eV) with good mobility (in theory about 400 cm²/V·sec) and an extremely high thermal conductivity (1.3 W/cm·K). GaN is also chemically inert and thermodynamically stable up to at least 600°C and probably higher. Its crystal structure is wurtzite with a=3.180Å and c=5.160Å lattice parameters and there exists a less studied cubic phase.

These properties make GaN an outstanding candidate for both optical and electronic device applications. Some possibilities are:

1. Lasers and LED's from the ultraviolet down through the visible spectrum.
2. Ultraviolet sensors.
3. High power devices.
4. Devices designed to operate in caustic or high temperature environments.
6. Protective coatings for semiconductor devices.

Despite its potential, GaN has received relatively little of the immense attention focussed on semiconductors over the past thirty years. Those who have made efforts towards realizing high quality GaN have been stymied by nitrogen vacancies which cause the films to be strongly n-type. Also, the lack of a substrate material which is both thermally compatible and a reasonable lattice match has hindered efforts. Those who have attempted to work with GaN material have found that there is no reliable way to pattern GaN films due to its chemical inertness. At the time, these problems were insurmountable.

It is the belief that technology and semiconductor processing techniques have progressed to a point at which these difficulties might be overcome which motivates our renewed efforts towards realizing device quality GaN layers. We have spent the first six months of our funding assembling the experimental apparatus which we believe will be able to produce GaN devices. We expect to begin producing GaN layers by the beginning of March. The following pages will outline in detail what we have assembled and how we intend to produce device quality GaN.
TECHNICAL APPROACH

Our technical approach divides itself into two stages. In the initial stage, our objective is to develop methods of preparing device quality single crystal epitaxial layers of GaN. In the second stage we will concentrate on realizing the vast potential of GaN for novel devices.

Studies towards an optimized deposition process will be carried out on an already existing Physical Electronics Series 430 Molecular Beam Epitaxy (MBE) system. The MBE system has been modified to handle gas sources and will hereafter be referred to as GSMBE. Detailed electrical and optical studies will be carried out at the Coordinated Science Laboratory. Structural characterization will be conducted at the adjacent Materials Research Laboratory, which incorporates the National Center for Microstructural Analysis and the National Center for Microchemical Analysis.

In our GSMBE system gallium is provided for growth by a conventional molecular beam. Nitrogen will be provided in an excited state by passing the gas through a electron cyclotron resonance aided microwave plasma source specially designed for the GSMBE. The plasma will produce ions and excited species of both atomic and molecular nitrogen that will have an increased reactivity at the substrate surface. Thus by experimenting with different ion/radical ratios we shall be able to explore a wide range of growth conditions. In situ high energy electron diffraction and residual gas analysis will allow us to analyze the quality of growth as it occurs as well as study the growth mechanisms of GaN in detail.

The selection of plasma enhanced deposition is based on the assumption that the relatively low resistivities \(10^{-2} \text{ to } 10^{-3} \ \Omega\cdot\text{cm}\) and high n-type carrier concentrations \(10^{17} \text{ to } 10^{19} \ \text{cm}^{-3}\), which characterize the single crystal GaN material deposited to date, are a direct consequence of a high level of nitrogen vacancies. Nitrogen vacancies are indeed the cause cited by virtually all those who have grown single crystal films\(^5\text{–}12\).

All single crystal GaN films grown to date have had wurtzite structure, with the exception of the NC State work of GaN on SiC.\(^13\) However, it is well known both theoretically and experimentally that GaN exists as a zincblende phase as well. It has a lattice constant of 4.51Å and...
a direct gap of roughly 3.4 eV. Indeed, the existence of the cubic phase has been confirmed by X-ray for MOCVD growth of GaN on GaAs (100) and (111) surfaces. All of the known cubic III-V semiconductors are amphoteric and it is possible that the cubic phase is also. We intend to further explore this phase, capitalizing on the non-equilibrium growth conditions available in MBE.

We intend to perform detailed electrical, optical, and structural measurements to determine the quality of our GaN layers. Hall measurements will determine the resistivity, mobility and carrier concentrations of our films. We plan to perform absorption, and reflectivity measurements in order to determine the bandgap, impurity spectrum, and exciton spectrum of GaN layers. Electron channelling, X-ray diffraction, and TEM observations will determine the crystallographic quality of our samples as well as the quality of our epitaxy. Deep level transient spectroscopy (DLTS) will give us information regarding traps and deep levels. In order to undertake optical studies of GaN, we plan to purchase a spectrophotometer which operates from the near ultraviolet through the visible spectrum. This will allow us to examine absorption and reflectance of pure and doped GaN.

There have been a moderate number of studies concerning the alloys of GaN. These include substitution of indium and aluminum in the group III position and phosphorus in the group V position. All of these studies have encountered difficulties similar to that of pure GaN studies, specifically nitrogen vacancy defects which lead to uncontrollably high n-type carrier densities. Successful growth of alloys will extend the spectrum obtainable with GaN based devices to photon energies of 1.9 eV through 6.2 eV (the band gaps of InN and AlN). It is likely that if we can overcome the difficulties in GaN we can do the same for indium and aluminum alloys and then we will enjoy a great deal of latitude for optical device design.

Another chronic problem encountered by groups researching GaN is that no wet chemical etch has proven successful at patterning GaN. Our group has recently purchased a Plasmatherm 700 reactive ion etching system (RIE). No investigator to our knowledge has applied this relatively new technology to GaN. Preliminary studies on gallium rich polycrystalline GaN samples grown
on glass (received from Prof. J. Greene) have shown complete removal of GaN by RIE. We are hopeful that RIE will be successful for etching the high quality single crystal material which we will be growing.

If high quality single crystal GaN can be grown, the possibilities for novel optical, electronic and acoustic devices abound. These include lasers, LED's, ultraviolet detectors, high power devices, devices designed for high temperature or caustic environment, negative electron affinity emitters, protective or passification layers for other III-V devices, and piezoelectric devices. A number of optical devices have already been demonstrated. One group has observed stimulated emission in the ultraviolet at 3.45 eV from single crystal GaN needles pumped with a pulsed N₂ laser. Numerous investigators have observed luminescence from MIS structures based on GaN.

GaN has a high thermal conductivity, good stability at elevated temperatures, is chemically inert, and has a hardness which exceeds that of sapphire. These properties make GaN devices and coatings suitable for use in high temperature and/or caustic environments as well as in high power applications. The combination of these properties along with its wide band gap, make GaN an excellent candidate as a passification layer for existing III-V devices as well as protective coatings. Also there are several preliminary studies available which predict that GaN may have applications for surface acoustic wave devices and negative electron affinity emitters.

All of the major efforts at developing GaN technology took place roughly fifteen years ago. Since that time, much progress has been made in the field of semiconductors which can be applied to GaN. The technology of MBE has reached maturity and it is time to apply it in new directions. New deposition techniques make low temperature growth feasible where previous investigators could only deposit polycrystalline layers at temperatures of 1000°C or more. Semiconductor processing has advanced along with deposition and it is possible that single crystal GaN layers can be patterned using reactive ion etching. It is our program to apply these techniques towards GaN to achieve high quality single crystal epitaxial layers. Once this has been accomplished, we shall take the natural next step of exploring the relatively untrodden area of GaN based devices.
ACCOMPLISHMENTS

In six months time we have assembled much of what is needed to carry out the proposed program. The two most important pieces of equipment are the Physical Electronics 430 gas source molecular beam epitaxy machine (GSMBE) and the nitrogen radical source made by Wavemat, Inc. We have assembled sufficient support equipment to begin growing GaN films immediately upon delivery of the nitrogen source.

The GSMBE is one of seven MBE machines in the Epicenter at the University of Illinois. GSMBE combines advantages of both conventional MBE and chemical vapor deposition (CVD). Specifically, GSMBE retains the ability to form sharp monolayer heterojunctions and has the excellent reproducibility of MBE growth techniques such as high energy electron diffraction and residual gas analysis. The beam nature of GSMBE eliminates viscous flow patterns which are present in CVD reactors while the gas sources eliminate the need to periodically open the system to replenish material.

The University of Illinois GSMBE will have lines for gallium, indium and aluminum based metalorganics as well as arsine and phosphine in the group V. Also, methane, silane, diborane and germane will be available as dopant. There are effusion cells for up to five elements so that solid source gallium, indium and aluminum will be available as well as arsenic and phosphorus from conventional cracker sources. The GSMBE is presently operational with conventional sources and crackers and awaits the delivery of the nitrogen radical source in the middle of February to begin deposition of GaN. The gas sources for As, P, Si, and Ge should be operational by Summer 1989.

The nitrogen radical source has been custom designed by Wavemat Inc. of Plymouth, MI for this specific application and machine. In the Wavemat design (Figures 1 and 2), gaseous nitrogen is fed into a microwave cavity where it is ignited into a plasma. Coupling between the microwave energy and the plasma is enhanced by a multicusp magnetic field created by eight permanent magnets in a symmetric arrangement about the discharge area. This arrangements sets up surfaces in which free electrons resonantly absorb the microwave energy through cyclotron resonance. This energy is given to the plasma in subsequent collisions of the electrons with the
ECR CAVITY CONFIGURED FOR
ION SOURCE APPLICATION

Figure 1
Figure 2
atoms and molecules. The resulting radicals diffuse thermally onto the substrate and should have an enhanced reactivity at the surface. It is expected that this higher reactivity will make significant gains towards eliminating the nitrogen vacancies in our GaN. Since the beam is neutral and thermal, there will not be any deleterious effects such as substrate charging and surface damage from accelerated ions as in conventional ion sources. Also, remote plasma processes take place at greatly reduced temperatures in comparison with conventional techniques. We believe that it is possible to grow GaN below 600°C, the temperature at which some investigators begin to see nitrogen liberation from GaN films. In fact, single crystal GaN films have been grown at 300°C by plasma enhanced MOCVD.

We have been able to devise an arrangement in which the radical gun fits into the sleeve of the MBE and emits the nitrogen at a distance of only eight inches from the substrate in favor of the twenty-two inch distance from the source flange to the substrate (Figure 3). This will limit losses in transport and eliminate recombination of atomic nitrogen on the walls of the cryoshroud. Thus we expect a very high flux of excited species to reach the substrate during growth. One final note, the radical source is by no means limited to nitrogen. We will have three lines feeding into the source, one of which will be dedicated to nitrogen, ammonia or hydrazine, one will be dedicated to hydrogen for GaAs passivation or substrate cleaning, and a third will be used for any other process gas desired, most likely a dopant.

It is the delay associated with this custom designed nitrogen radical source which has kept us from initiating GaN growth earlier. Wavemat assures us that delivery will occur Monday, February 13, 1989 at which time we can install the radical source on our GSBME system.

The nitrogen source is the heart of our research program, so it has been impossible to begin producing layers. However, all of the support equipment necessary for GaN deposition is in our possession. We have assembled a gas delivery system for the Wavemat source. The gas delivery system draws gaseous nitrogen from liquid boil-off. This gas is then filtered to extremely high purity and introduced to the source through a leak valve. The RIE machine is well characterized for GaAs and has even been used on a low quality layer of GaN with success.
We have also ordered an electron cyclotron resonance plasma source of slightly different design from Conversion Technology. This design has an axial magnetic field which is approximately uniform throughout the plasma. Thus the entire discharge area can be tuned for cyclotron resonance which should improve coupling to the plasma. Such a field arrangement was impossible in the Wavemat source since we desired the radical gun to fit into the sleeve of the GSMBE thereby minimizing plasma losses in transport. The Conversion Technology radical source will be installed on our low pressure CVD chamber adjacent to the GSMBE and be used to grow SiC and MgO substrates for our GaN work. SiC has the closest lattice match to GaN of any reasonable substrate material and permits nearly strain free growth. The fact that SiC is semiconducting makes it a candidate for fabrication of heterojunctions with GaN. Our setup allows us to pass substrates under vacuum from one chamber to the other and we will have hydrogen radical surface cleaning capability in both chambers.

A great deal of effort has also been expended characterizing our new GSMBE machine. The system was signed off in October 1988 and has required a number of minor repairs. We have been growing layers on a regular basis now for the past two and one half months and we expect research quality material to be produced soon. Thus the anticipated delivery of the Wavemat radical source coincides well with the development of our GSMBE system and we should soon be making rapid progress.

We have a large number of ideas which we wish to explore. Our laboratory's outstanding facilities and flexibility will allow us to attempt a broad range of growth conditions. We can attempt any alloy of GaN with In, Al, As, and P at extremely low growth temperature due to our plasma nitrogen source and our other gas sources. Foremost in our device objectives is the realization of solid state devices which operate in the ultraviolet including lasers, LED's and photodetectors. Utilizing different alloys we hope to make devices active from the visible spectrum well into the ultraviolet. Once we can deposit epitaxial GaN on GaAs we hope to capitalize on the high thermal conductivity and wide band gap of GaN and use it as a passification layer for our high speed device work. We will also explore uses of GaN as a protective coating for semiconductor devices for operation at high temperatures and in caustic environments.
It is apparent that GaN is a material of enormous potential. We have numerous plans for our research and anxiously await its commencement. Up to this date we have done all we could do to prepare for the delivery of our nitrogen radical source and we have every reason to expect preliminary results soon after delivery.
REFERENCES

13. Private Communication through Max Yoder.
30. Pankove, Miller and Berkeyheiser, J. Lum. 5, 84 (1972).