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# Nitrogen plasma optimization for high-quality dilute nitrides

Mark A. Wistey, Seth R. Bank, Homan B. Yuen, Hopil Bae, James S. Harris Jr.*

*Solid State & Photonics Laboratory, Stanford University, CIS-X 328 Via Ortega, Stanford, CA 94305-4075, USA*

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## Abstract

Growth of GaInNAs by molecular beam epitaxy (MBE) generally requires a nitrogen plasma, which complicates growth and can damage the wafer surface. Optical spectra from both ends of the plasma cell were nearly identical, and were found to be insensitive to certain changes in the cell condition evidenced by a change in reflected RF power and stability. A slight amount of excess capacitance in the matching network improved stability, particularly while the cell warmed up. Furthermore, despite steps to reduce the ion flux from the plasma, a remote Langmuir probe showed significant ions. Moderate voltages on deflection plates were sufficient to remove these ions, with a 3–5× increase in photoluminescence resulting from 18–40 V deflection.

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## 1. Introduction

The development of GaInNAs by Kondow [1] has allowed unprecedented wavelengths on GaAs, leveraging mature fabrication technology and high-contrast GaAs/AlGaAs layers for vertical cavity surface-emitting lasers (VCSELs). Until recently, however, the quality of dilute nitrides lagged behind that of comparable InGaAs and InGaAsP lasers.

This paper addresses several of the challenges of plasma-assisted molecular beam epitaxy (MBE) of high-quality dilute nitrides, such as finding a stable operating point with minimal ion production. Minimizing the reflected power does not necessarily lead to the most stable operating point of the cell. Remote Langmuir probe measurements show that a significant ion flux persists even after taking steps to reduce it. This ion flux causes damage to the wafer surface during growth, but moderate voltages applied to parallel plates placed across the exit aperture of the plasma cell are sufficient to deflect the ions from the plasma beam. As a result

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*Corresponding author. Tel.: +1 650 725 8313; fax: +1 650 725 4659.
*E-mail addresses:* wistey@snow.stanford.edu (M.A. Wistey), sbank@snow.stanford.edu (S.R. Bank), harris@snow.stanford.edu (J.S. Harris Jr.).

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of the optimizations in RF matching, aperture, and deflection voltages, we were able to demonstrate the first cw, room temperature lasers on GaAs beyond 1.5 μm [2], and the first GaAs-based VCSELs at 1.46 μm [3].

## 2. Optimization procedures

### 2.1. Optical emission spectra

To create reactive nitrogen for MBE growth of nitrides and dilute nitrides, inert $N_2$ molecules must be cracked using a plasma. The measurements below were performed on a Varian Mod Gen II MBE system, with an SVT Associates Model 4.5 RF nitrogen plasma cell operating at 300 W RF power and 0.5 sccm of ultrapure nitrogen gas. Ions, atoms, and excited molecules produce characteristic features from the near-UV to the near-infrared [4,5], as shown in Fig. 1. Thus, optical spectra are useful as a rough guide to finding the best combination of gas flow, RF power, and RF matching to produce a high cracking efficiency. Two spectra are shown, one from a fiber bundle butt-coupled to the rear viewport with line of sight to the plasma, and the other imaged onto the pinholes in the front PBN aperture using an $f = 0.5\,\mathrm{m}$ lens. The general shapes of the two spectra are nearly identical, as shown by the difference between them, also plotted in Fig. 1. A quartz viewport may allow the study of ion emission from 300 to 500 nm, but our fiber bundle was only weakly transparent to UV.

Series and parallel capacitors were used to compensate the inductance of the RF plasma. With excess capacitance, however, the intensity of various spectral features decreased, as shown in the lower set in Fig. 2. For this measurement, the series capacitance was increased until the reflected power reached 10 W. Although this is a modest 3% of the total RF power, the atomic emission lines were reduced by nearly 20%, and the molecular bands reduced by nearly 5%. This demonstrates the need to maintain constant net RF power for stable output in this regime. For example, if the minimum reflected power were to drift from 0 to 5 W, then the forward power would need to be increased by 5 W. Upon increasing the forward power, the various emission features roughly returned their original intensities (not shown).

However, optical spectra can also be misleading. The upper set of features in Fig. 2 are nearly unchanged even though the cell is operating in an unstable regime; the plasma died soon after this measurement. If the cell drifts toward this condition, monitoring the optical emission

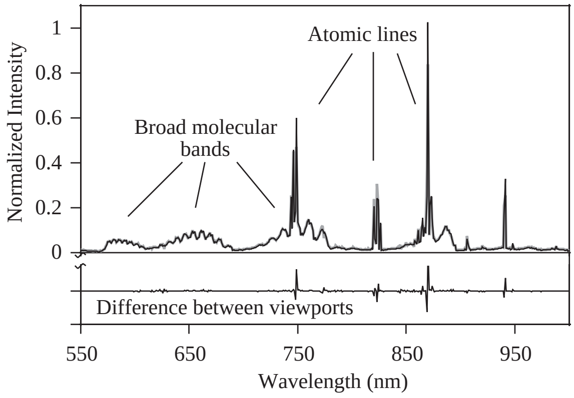

Fig. 1. Plasma optical emission from front aperture (thick grey line) and rear viewport (thin black line) are virtually identical. The difference is plotted below using the same scale.

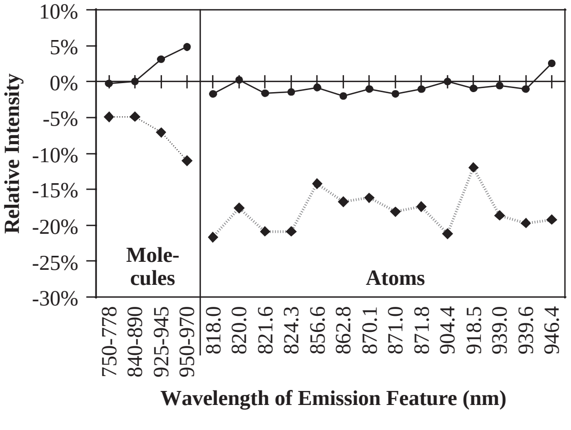

Fig. 2. Emission features from 750 to 950 nm, relative to matched condition. The matching capacitor was detuned for 10 W of reflected RF power, with either insufficient or excess capacitance (top or bottom curves, respectively).

spectrum will not provide sufficient warning of cell instability.

The total intensity of emission can likewise be misleading. The overall intensity of the plasma is dominated by very strong atomic lines, particularly near 869 nm. However, excited molecular nitrogen can also contribute significantly to nitride and dilute nitride growth [6,7]. Under certain conditions, the density of excited molecular species can increase while the atomic species decrease or vice versa. It is not sufficient to monitor the total intensity of emission, nor a single set of atomic lines [6], except as a baseline to detect gross changes in the cell. Similarly, changing the RF power or gas flow merely to change the rate of nitrogen incorporation raises a number of variables that are not easily resolved.

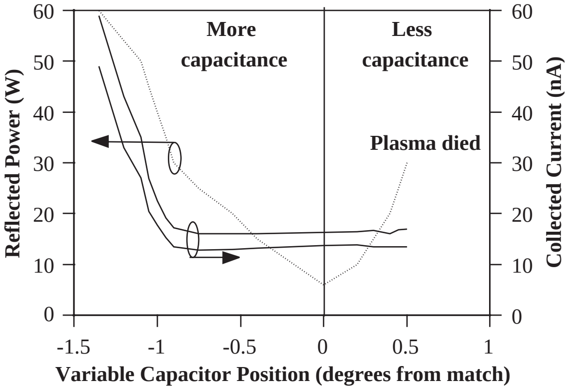

Fig. 3. Current collected by two grounded deflection plates (solid lines) vs. matching capacitor position, showing a "bathtub" shaped stable region. Dashed line shows reflected RF power. Current and reflected power rose sharply just before plasma died.

### 2.2. *RF matching and cell stability*

The stability of the plasma is especially critical for VCSELs and careful materials studies. The above optical measurements showed an asymmetry in the operation of the cell with respect to the variable capacitor on the matching network. With excess series capacitance, the plasma grew somewhat dimmer but continued to operate in H-coupled mode (high intensity), even with reflected powers as high as 65 W. But if the capacitance was decreased below the matched condition, the plasma rapidly became unstable and either dropped into an E-coupled mode (low intensity) or extinguished completely, usually before the reflected power reached 30 W. The existence of the asymmetry was corroborated from current measurements at the deflection plates mounted across the output of the cell. Fig. 3 shows the current collected through the two grounded deflection plates as a function of the matching capacitor position.

Using an automatching network or continually monitoring the cell to make sure it remains impedance matched, the plasma can be kept in a stable operating range. However, an extra cushion of stability may be provided by a slight amount of excess capacitance at the matching network.

The excess capacitance is particularly useful as the cell stabilizes. After igniting the plasma or making a major change to its operating point, such as increasing the RF power, it takes up to 15 min for the cell to reach a stable, steady state. This is likely due to heating in the matching network, and cells from other major vendors have displayed the same behavior [8]. Fischer reported the use of a gate valve to separate the plasma from the chamber while the cell was warming up [9]. But a gate valve can itself lead to instability, either by inductive loading or by changing the pressure in the plasma cell [8]. In short, some provision must be made to allow the plasma to stabilize before starting each growth [10].

In addition to the warmup delay, the plasma often behaves somewhat differently during the first run of the day. There appears to be a significant benefit in cell stability, ease of lighting, and lower reflected power if the plasma is operated (seasoned) immediately before growths begin. We believe that the principal effects of seasoning are to establish a thermally steady state, and to evaporate deposited arsenic from the crucible.

Other technical problems related to RF plasma sources have included transients when the metal MBE shutter is opened, and RF leakage interfering with the mass flow controller. These are beyond the scope of this paper.

### *2.3. Deflection plates and remote Langmuir probe*

The final aspect of cell optimization was limiting ion damage from the plasma. RF plasmas generate fewer ions than ECR or arcjet plasmas, while still demonstrating a high cracking efficiency [11]. Kageyama reported that the ion density saturates with increasing RF power [7]. However, at high RF power or low flow rates, the energy per atom climbs, and the ion density rises again. But high power and low flow rates also produce desirable atomic nitrogen. To minimize ion generation, a small cell aperture is used to raise cell pressures, neutralizing ions and stripping energy from the higher energy radicals [7,11,12]. In addition, Blant reported that hot walls of the plasma chamber would lead to negligibly small fluxes of ions, less than 1 nA [6]. The remaining ions could easily be removed by magnets [13] or ion deflection plates [7]. Several samples were grown using ±800 V deflection plates but failed to show a substantial improvement in photoluminescence (PL), and it appeared that ions were indeed negligible, yet laser threshold currents were extraordinarily high.

To measure our ion flux directly, we attached a picoammeter between ground and the MBE beam flux monitor ion gauge filaments, forming a Langmuir probe. A DC bias separated electron current from ions. This simple, convenient technique offers a more complete picture of the plasma flux at the actual wafer position. Details will be provided elsewhere [14,15]. A typical *I–V* curve is shown in Fig. 4. We found that the ion flux from the plasma was indeed greater than 1 nA. The highest energy ions ranged in energy up to 35 eV. Electron energies were under 8 eV, consistent with other reports for RF plasmas. The large slope of the saturation current is due to secondary electrons, and remains linear at higher voltages.

We determined that −40 V applied to one deflection plate was sufficient to remove the majority of ions from the plasma. PL from GaInNAsSb quantum wells improved by a factor of 3–5×, as shown in Fig. 5. PL at 300 and 15 K showed significantly better material, as did reflection high-energy electron diffraction (RHEED), and nuclear reaction analysis Rutherford backscattering spectroscopy (NRA-RBS) showed significantly reduced nitrogen interstitials after annealing.

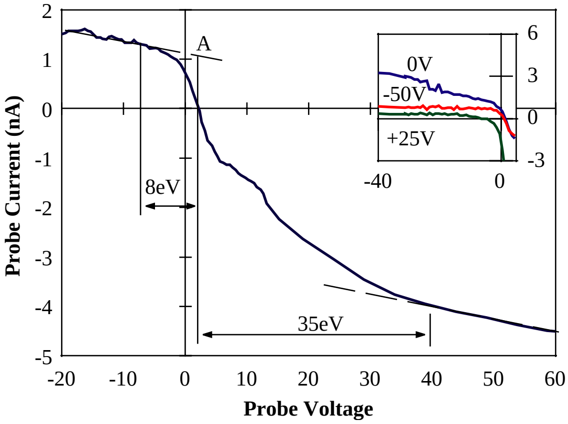

Fig. 4. Langmuir probe at wafer position. Saturated ion current, at A, is ~ 1 nA. The most energetic electrons and ions are 8 and 35 eV, respectively. Inset: saturated ion current for various deflection voltages.

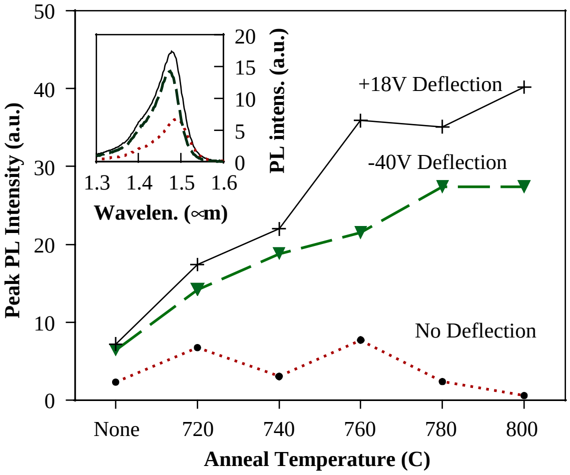

Fig. 5. Peak PL intensity increases 3–5× with moderate deflection plate bias.

There was some early concern that the deflection plates were close enough to the plasma that very large electric fields could perturb the plasma itself. However, there was no change in reflected power or thermocouple temperature with deflection bias, and less than 1% variation throughout the spectrum, even with deflection voltages as large as 1000 V.

## 3. Conclusions

We have presented some of the techniques of plasma operation which we have found to be instrumental for growing high-quality dilute nitrides. The stable operating window is not centered at the lowest reflected power, but is slightly (0.1%) on the side of excess capacitance. Allowing the cell to warm up and stabilize before growth is necessary for repeatable results, as is a "seasoning" run before the first growth of the day. Optical spectra are insensitive to some signs of plasma fluctuation but exaggerate others. Finally, using the beam flux monitor as a Langmuir probe, we found ion currents of 1 nA, at energies up to 35 eV. Although high voltages on the ion deflection plates (±800 V) failed to improve material quality, a remote Langmuir probe allowed the selection of suitable voltages on the deflection plates to remove these ions, yielding a 5× improvement in PL intensity. These techniques together have enabled record long-wavelength dilute nitride lasers and VCSELs grown on GaAs.

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