1. COVER PAGE

Texas Space Grant Consortium

FINAL REPORT

Project title: Compact III-V Nitrides-Based Integrated Multifunctional Optoelectronic Sensors for Contaminant Characterization in Enclosed Space Environments.

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Abstract

Our objective was to implement the technology developed during the first year of this project to the fabrication of nitride-based optoelectronic sensor structures on silicon wafers. This objective has been reached through optimization of the MBE process, the Reactive Ion Etching (RIE) and device fabrication techniques. Control of the RIE process was improved using a miniature ORthogonal extraction Time of-Flight (ORTOF) mass spectrometer, developed by our collaborator Ionwerks, and Optical Emission Spectrometer (OES).

RESULTS

A: Growth Issues

High quality p-GaN layers were required for optoelectronic sensor p-n heterojunctions fabrication. To that end we studied the incorporation of Mg during RFMBE film growth. This study was performed in-situ by RHEED and ex-situ by SIMS, Van der Pauw-Hall effect, hot-probe method, and electro-chemical C-V measurements.

Three different regions of growth parameters were identified. In the first region the Ga to N flux ratio was higher than 1 and Mg had an extremely low incorporation rate. Under Ga-rich conditions, blocking/masking of Mg incorporation sites by a metallic Ga surface layer probably lowers Mg incorporation. The second region was defined where the Ga to N flux ration was slightly smaller than 1. The transition between the Ga-rich and N-rich regimes is illustrated in Figure 1a by the SIMS profile taken from a sample grown at 750°C. There is a clear increase in the amount of Mg in the film as the gallium flux is decreased corresponding to the transition between Ga-rich and N-rich regimes. The third region was defined by a Ga to N ratio significantly below unity. As indicated in Figure 1b the Mg incorporation was strongly dependent upon the Mg flux in this regime. At some critical Mg to Ga ratio there is a change in the growth mode which leads to a reduction of the Mg incorporation in the remaining film. Layers grown with fluxes below this critical value were conductive and strongly p-type by hot probe. Layers grown above the critical value, however, were mostly insulating and very weakly p-type by the hot-probe method.

Ideally, hole concentrations in the rage of $5x10^{17}$- $1x10^{18}cm^{-3}$ would be optimal for light-emitting devices in order to enhance the recombination process in the sensor structure at forward bias. However, lower hole concentrations in the range of $1x10^{17}$- $5x10^{17}cm^{-3}$ provide high electric fields (>10 V/μ m) which enhance the avalanche electroluminescence process. Therefore results on RFMBE growth of GaN:Mg have achieved an appropriate doping level for optical emitters and sensors.

The second task in integrated optoelectronic sensor development was the growth of AlGaN layers. A series of experiments was performed in order to grow $Al_xGa_{1-x}N$ layers with various Al mole fractions on (111) Si wafers. These samples were analyzed by room-temperature cathodoluminescence (CL) in order to determine the Al content in the $Al_xGa_{1-x}N$ layers. The resulting spectra are shown in Figure 2 and reveal Al fractions ranging from x=0.07 to x=0.42 with the assumption of a band bowing parameter of 1eV. Besides the employment of AlGaN layers with various Al fractions in passive optical filters based on optical interference in multiple quarter-wave layers with various refractive indexes, such layers can be employed in our sensors as active layers for light emitting diodes with an UV-extended spectral range.

The third step towards integrated sensor development was the growth of insulation AlN layers. Based on its bandgap of 6.2eV, AlN should be an excellent insulator at room temperature and have high breakdown fields. However, most AlN layers tend to break down well before their theoretically predicted value. We have performed a series of experiments to determine the optimum conditions for insulating AlN growth on (111) Si substrates. These conditions were determined by balancing the conflicting requirements of using the lowest substrate temperature to minimize Si diffusion while keeping the substrate temperature high enough for deposition of crystalline AlN. For this purpose AlN layers were grown at substrate temperatures in the range from 545 to 750°C. In order to measure the electrical properties of the films, 1 mm diameter Al dots were deposited on these samples by vacuum evaporation. The I-V characteristics were measured between the Al dots and the conductive Si wafer. Those samples grown at temperatures below 625°C exhibited high leakage currents at low voltages, most likely due to the poor crystalline quality of the layers. Samples grown above 670°C were also very leaky, possibly due to the diffusion of Si. Ultimately a 1200Å thick AlN sample grown at 650°C exhibited a breakdown voltage of 40V (Figure 3) that corresponds to a breakdown electric field of

333V/μ m. This is adequate for our applications.

B: Prototype Development

We have also fabricated two multifunctional optoelectronic sensor prototypes. Using the prototypes we have measured fluorescence from a Fluorescein™ dye in methanol solution and with different pH values (Figure 4A). Also, fluorescence was measured from chlorophyll extracted from three groups of green leaves (Figure 4B). The detection limit in these measurements was limited by a background signal resulting from the direct illumination of the photodiode from the LED through the sapphire substrate and by light scattered by other components. Enhancement of the signal, achieved by placing a metallic mirror in front of the sapphire substrate, allowed measurements based on: a) optical absorption in potassium and cobalt salts (Figure 4C); b) variation of the refractive index of commonly used organic solvents (Figure 4D); c) scattering by alumina powders of various sizes (Figure 4E). These results indicate that several sensor functions can be achieved using the same component setup.

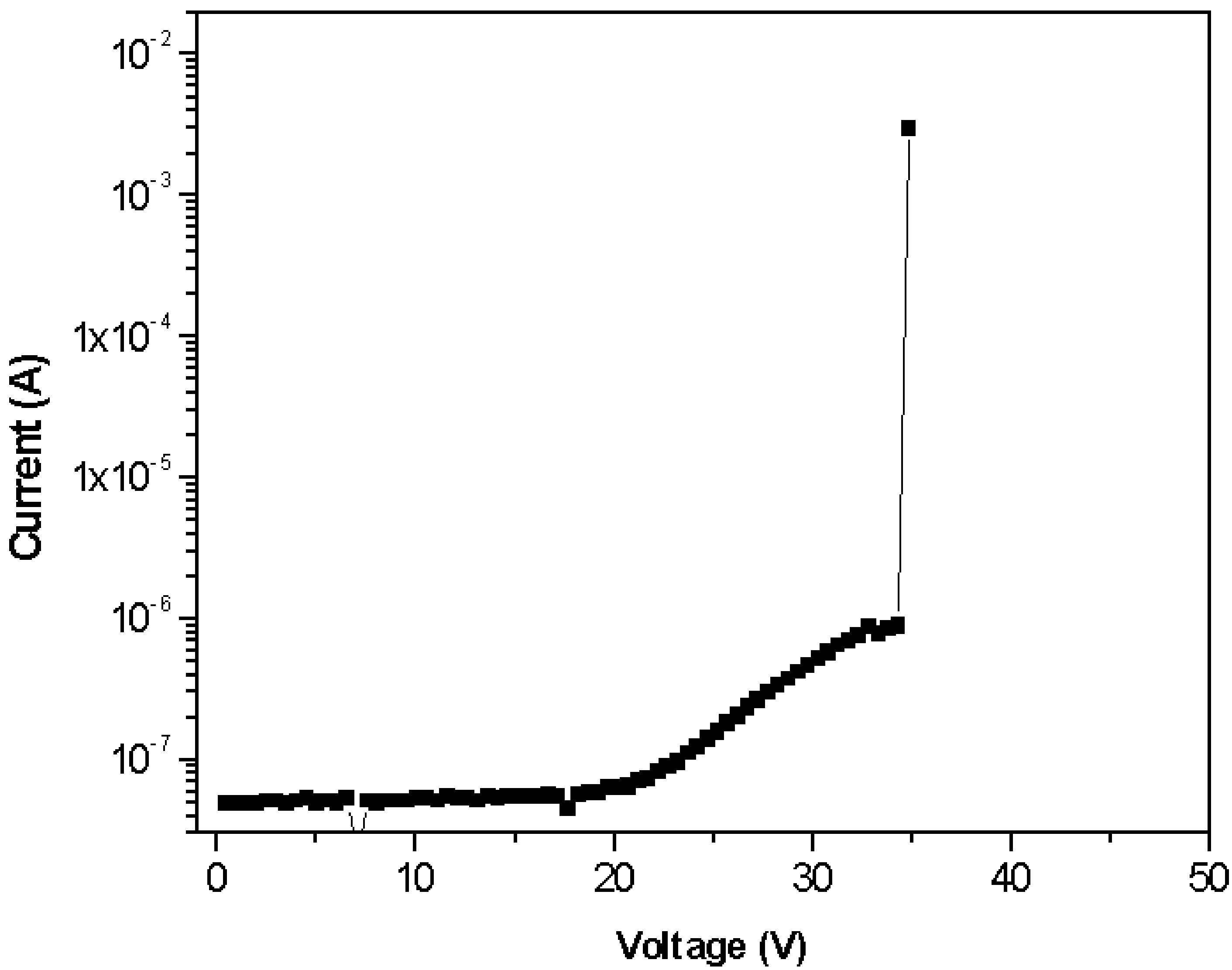
C: Processing Technique Optimization

As part of this project we have also continued development of the RIE process using the ORTOF mass spectrometer (Ionwerks, Inc). Initial MS tests with the instrument were performed using different process parameters (gas mixture, RF power, pressure and illumination). Product species such as $^{28}Si^{35}Cl$, $^{28}Si^{35}Cl^{37}Cl$ and $^{28}Si^{35}Cl_2$ were detected from Cl_2/Ar plasma during the etching of silicon. The GaN RIE and PA-RIE processes using the same chemistry were also monitored. Photoenhancement of the observed peaks including those of etch product $^{14}N^{35}Cl_3$ were observed.

The second part of the RIE improvement involved optical emission spectroscopy for end-point detection during the dry etching of III Nitride multi layers such as those employed for the optoelectronic sensor fabrication. An Ocean Optics PC 2000 UV-VIS miniature fiber optics spectrometer having a resolution of 1.5 nm (FWHM) was used to analyze emission lines from the plasma. The optical emission spectra from RIE and PA-RIE $BCl_3/Cl_2/N_2$ plasmas during GaN etching at a 200 W RF power are shown in Figure 5. The process parameters were 30 mTorr reactor pressure, 200 W RF power corresponding to a dc bias of –310 V, 10 sccm BCl_3, 10 sccm Cl_2, and 10 sccm N_2. OES lines obtained in this case were GaCl (337 nm), N_2 (358 nm), BCl_3 (271 nm), Cl_2 (256 nm), and BN (385.6 nm) with many weaker emissions (Cl^+ at 413 nm, Cl at 726, 741, 755, 775, 808.3, and 837.5 nm). Emission intensities increased with increasing RF power (from 100 to 300 W). The GaCl emission line intensity, for example, increases slightly from 100 to 200 W, then has a higher linear rate increase from 200 to 300 W (Figure 6). Etch rates also follow the same pattern, making possible the use of this line as endpoint detection in etching GaN with non-gallium containing materials. Higher emission intensities were obtained in the PA-RIE process at 200 W RF power, demonstrating photo-enhancement of the etch process using these conditions (Figure 5). This corroborates our previous etch rate results where maximum photo-assisted to standard etch ratio (4.4) was obtained at 200 W RF power.

D: Conclusions

In this project we have demonstrated that GaN emitter-detector pairs can be fabricated and utilized as sensitive chemical sensors. Using fluorescence, adsorption and reflection spectroscopy we have determined the concentration and optical characteristics of various analytes. Implementation of ORTOF-MS and OES techniques in a RIE reactor allowed for improved controlled of the etch process and confirm our previous results concerning enhanced etching under light illumination.



10-2
10-3
1x10-4
1x10-5
10-6
10-7
Current (A)
0
10
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40
50
Voltage (V)

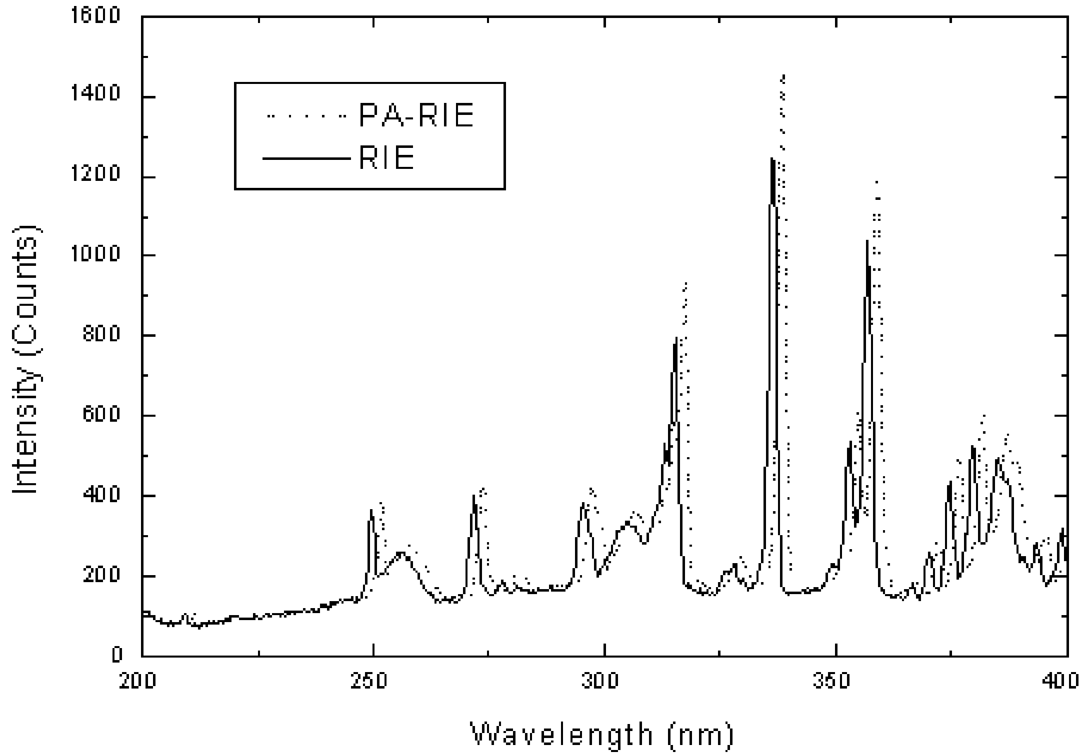

Figure 5. OES spectra of GaN $BCl_3/Cl_2/N_2$ RIE and PA-RIE plasmas (the PA-RIE curve was shifted by 2 nm for illustrative purpose).

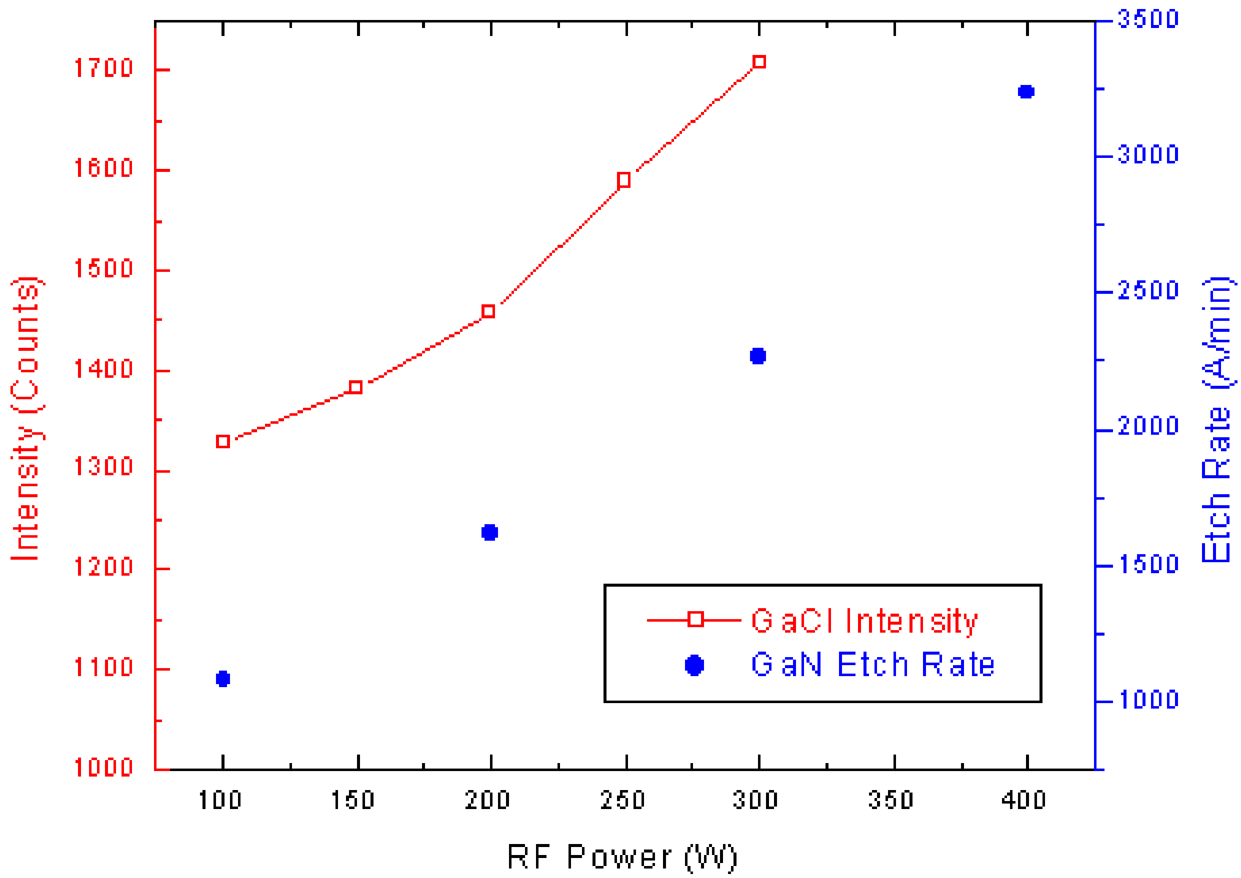

Figure 6. GaCl emission line (337 nm) intensity (left) and GaN etch rate (right) vs. RF power during the RIE of GaN in $BCl_3/Cl_2/N_2$ at 30 mTorr.

E: Publications and Presentation Acknowledging TSGC Support

Reviewed Pubilcations:

1. D. Starikov, C. Boney, I. Berishev, I.C. Hernandez, and A. Bensaoula. Radio-frequency molecular beam epitaxy growth of III nitrides for microsensor applications. J. Vac. Sci.Tech., B 19(4), 1404- 1408, (2001)

2. D.Starikov, C. Boney, J-W.Um, N. Medelci, and A. Bensaoula. Development of Integrated Optoelectronic Sensors Based on III Nitrides" (To be published in JVST in 2002)

Conferences:

1. N. Medelci, A. Tempez., D. Starikov, N. Badi, I. Berishev, and A. Bensaoula; Photoenhanced Reactive Ion Etching of III-V Nitrides in BCl3/Cl2/Ar/N2; Material Research Society Spring Meeting, April 5-9 1999, San Francisco, CA.

2. D. Starikov, E. Kim, C. Boney, I. Hernandez, I. Berishev, J.-W. Um, and A. Bensaoula. RF-

MBE Growth of III-Nitrides for Micro Sensor Applications. 19th North American Molecular Beam Epitaxy Conference, Tempe, AZ, October 15-18, 2000.

3. D. Starikov, C. Boney, J-W. Um, N. Medelci, and A. Bensaoula. Development of Integrated Optoelectronic Sensors Based on III Nitrides. 48th American Vacuum Society International Symposium. San Francisco, CA, Oct.28-Nov.2, 2001