

Time of Flight Mass Spectroscopy of Recoiled Ions Studies of Gallium Nitride Thin Film Deposition by Various Molecular Beam Epitaxial Methods

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Gallium Nitride (GaN) thin films were successfully grown by electron cyclotron resonance molecular beam epitaxy (ECR-MBE), gas source MBE (GSMBE), and chemical beam epitaxy (CBE). Time of flight mass spectroscopy of recoiled ions (TOF-MSRI) and reflection high energy electron diffraction (RHEED) were used in-situ to determine the surface composition, crystalline structure, and growth mode of GaN thin films deposited by the three MBE methods. The substrate nitridation and the buffer layers were monitored and optimized by TOF-MSRI and RHEED. For GSMBE, the gallium to nitrogen ratio is found to correlate well with ex-situ optical properties. In the case of CBE, carbon incorporation determines the surface morphology, crystalline quality and optical activity of the epilayers.

1 Introduction

1.1 Time of Flight Mass Spectroscopy of Recoiled Ions

With many interesting and useful applications, GaN has become one of the most important optoelectronic materials. Among the GaN thin film growth methods, molecular beam epitaxy (MBE) growth has become a recognized technique for fabricating state-of-the-art short wavelength opto-electronic devices, although metal-organic chemical vapor deposition currently remains the technology of choice for producing the majority of GaN-based devices. [1], [2] Nevertheless, MBE is expected to be superior in terms of composition, thickness, doping, and interface control due to the beam nature of the source fluxes and the availability of various in-situ monitoring tools. In addition, the lower growth temperatures and the absence of residual impurities in the process should allow hetero-structures with controllable doping profiles, lower defect densities.

Although GaN LED and laser diodes have been developed recently, the precise growth mechanism and the role of substrate nitridation and buffer layers are not yet clearly understood. Both substrate nitridation and buffer layer growth dramatically improve the quality of the GaN layers on the highly mismatched sapphire sub-

strate. [3], [4] It is generally accepted that the nitridation step provides a better template for GaN nucleation and the thin low temperature GaN or AlN buffer layers relax the interfacial stress.

Ion scattering spectroscopy (ISS) is a well-established probe based on ion-solid interactions. A variant, called low energy ion scattering (LEIS) by time-of-flight (TOF) detection, is a powerful technique for surface structural and elemental analysis. [5] This technique has been proven as a real time thin film growth monitor in background pressures up to 10^{-2} torr [6], [7] and, therefore, can be particularly useful for studies of gas source MBE growth of GaN. It does not induce any measurable damage in the thin films due to the extremely low ion beam current densities used (as low as $\sim 10^{10}$ primary ions/cm²). [8] The technique is essentially nondestructive. Since TOF-LEIS spectra are nearly independent of the chemical environment, there is a minimum matrix effect in contrast to secondary ion mass spectroscopy (SIMS). A recently developed ISS technique, known as mass spectroscopy of recoiled ions (MSRI), has a better sensitivity (10^4 times higher for nitrogen detection) to light elements than SIMS, and superior minimum detection levels of $\sim 10^{17}$ ions/cm³. [9] In addition, the low incidence angle of TOF-MSRI

makes it suitable for real time surface analysis in an MBE environment. As a surface probe, TOF-MSRI is an ideal in-situ complementary technique to RHEED.

GaN thin films were grown in our laboratory by different MBE techniques with various Ga and N sources. At first, ECR plasma assisted MBE technique was employed. In this method, activated nitrogen gas was supplied from an ECR plasma source. Elemental Ga was evaporated from a Knudsen cell. Next, gas source MBE GaN deposition was investigated using NH_3 and Ga. There is no need for excitation of the source molecule in this method. Ammonia gas is easily dissociated on the hot sample surface. Finally, chemical beam epitaxy (CBE) was utilized. In the CBE method, triethyl gallium (TEG) and ammonia were used as precursors.

2 Experimental Procedure

2.1 Sample Preparation

GaN thin films are grown on 0.01–0.02 inch thick, 1-inch diameter basal plane sapphire single crystal wafers. Before introduction into the load lock chamber, the samples are prepared in the following fashion. They are degreased with tri-chloroethylene, acetone and methanol, and rinsed with doubly de-ionized water. The substrates are then chemically polished in hot 3 H_2SO_4 : 1 H_3PO_4 by volume ratio in an acid mixture, rinsed in deionized water and nitrogen blow-dried.

2.2 Thin Film Growth and In-Situ Analysis

After this wet cleaning, the samples are mounted on an indium free 1-inch diameter sample holder. The samples are inserted into the introduction chamber where they are left until the pressure drops to the 10^{-7} torr range. The sample is then transferred to the manipulator in the main chamber where it is annealed in vacuum to 850 °C for 30 minutes. This process allows removal of residual hydrocarbons, oxides, and most other contaminants from the sample surface. This thermal cleaning is monitored by TOF-MSRI and RHEED. In this manner, the crystal structure and composition are known before each growth. In particular, the H, Al, O, C and any other impurities are monitored by TOF-MSRI. At this point, the sample's temperature is lowered to that appropriate to nitridation (600–750 °C), and either ammonia or ECR- N_2 is let into the chamber. Following nitridation, a low temperature buffer layer is deposited at 450–550 °C with either ECR-MBE (ECR- N_2 and Ga), GSMBE (NH_3 and Ga), MOMBE (ECR- N_2 and TEG), or CBE (NH_3 and TEG). Finally the sample is heated to the appropriate final epilayer growth temperature (750–850 °C) and the epilayer deposition is initiated. At the end of the growth, the sample's temperature is lowered gradually under a group V over-pressure. If no post growth

in-situ characterization experiments are planned, the sample is removed from the reactor.

3 Results and Discussions

3.1 ECR MBE

The ASTeX[®] compact ECR source was developed specifically for MBE applications. The ECR can be operated in a vacuum environment in the 10^{-5} – 10^{-4} torr range. In this range, the mean free path is about 1 meter, which is much longer than the source to substrate distance thus molecular flow regime is maintained. With ECR nitrogen source, degradation of the hot effusion cells and PBN sample heater is significantly lower than in case of ammonia.

Various energetic nitrogen species (N_2^* , N_2^+ , N and N^+) are generated in an ECR source. The effect of ion damage during MBE growth of GaN using plasma sources of active nitrogen is well documented. Several methods have been attempted to reduce or even eliminate this effect. For plasma sources there are: positive bias of substrate or grid, external transverse magnetic field, and modified ECR plasma exit aperture. [10], [11] Using this method, GaN films at growth rate as high as 1 $\mu\text{m/hr}$ were obtained. [12]

3.1.1 Substrate Nitridation

Sapphire (Al_2O_3) substrates were nitridated under ECR nitrogen plasma for 20–30 minutes to create an AlN template for subsequent GaN nucleation. The oxygen atoms in the topmost layers can be substituted by the nitrogen atoms supplied by the nitrogen ECR plasma source. For these experiments, the applied nitrogen gas flow was 3 sccm and the corresponding chamber pressure was 1.7×10^{-4} torr. The microwave power was 200–250 W and the current setting on the electromagnet power supply was 17–18 A. In a standard configuration, the ECR was fitted with a 3/8-inch diameter boron nitride (BN) aperture placed at the source exit. Such an aperture increases the pressure in the plasma region and allows easy ignition and stable plasma condition.

First, the nitridation efficiency was investigated as a function of sample temperature. A thermally cleaned sapphire substrate was nitridated for 10 minutes at each temperature. The temperature was varied between 550–850 °C. A TOF-MSRI spectrum was taken after each exposure. The TOF-MSRI results, the relative peak intensity (surface coverage) of the surface atoms, are presented in figure 1. A weak nitrogen peak was detected above 650 °C and increased when the sample was further nitridated at 700 °C. The onset of nitridation of sapphire was only identified by RHEED for a sample temperature above 700 °C. TOF-MSRI is thus a more

sensitive probe to optimize the substrate nitridation process.

While the previous experiment allowed determination of the optimum nitridation temperature, in the following we investigated the effect of exposure time at a constant ECR power of 200 W and a substrate temperature of 700 °C. We did not find degradation of nitridated surface – partially covered Al₂O₃ by crystalline AlN – when substrate surface was nitridated at higher temperature determined by in-situ RHEED and TOF-MSRI. However, usually we perform nitridation at the minimum required temperature to avoid unnecessary heat supply that may reduce sample heater's lifetime. Previous reports suggest that too short or too long a nitridation time resulted in the deterioration of the GaN epilayer quality. [3] To that end, an annealed sapphire surface was exposed to the ECR source, and the TOF-MSRI spectra were taken at 10-min intervals. In figure 2, the TOF-MSRI spectra at each interval are plotted. After a 20-min exposure time, the N signal is saturated. The carbon signal, however, continues to decrease with exposure, which implies ECR plasma is effective not only for the nitridation but also for cleaning a substrate. RHEED showed that an overlapped diffraction pattern of AlN and Al₂O₃ due to a thin AlN over layer on the sapphire substrate. A nitridated AlN layer remained as a single crystal up to 30-min exposure. No significant change is seen after a 30-min ECR plasma exposure by in-situ measurements.

3.1.2 Buffer Layer

Low temperature GaN buffer layers were grown by ECR-MBE at various growth temperatures. Typical deposition time for these buffer layers was 30 minutes, which resulted in GaN layer thickness in the range of 300–500 Å. RHEED from these layers show single crystalline surfaces for a growth temperature of 500 °C.

The streaky RHEED patterns were obtained, and they were remained unchanged when these layers are annealed to 750 °C under an ECR-N₂ beam. Also the buffer layers' crystallinity seem to be insensitive to the substrate nitridation time for 30 min. TOF-MSRI was utilized to survey the surface composition of the sapphire substrate after nitridation and during buffer layer growth. Figure 3 shows the elemental composition at four different times. The nitridated surface shows only N, O, and Al and no other contaminants. Immediately following the start of the buffer layer growth, the Al signal drops significantly. The buffer layer seems to proceed in a two dimensional growth fashion. Within five minutes, the Al and O signals completely disappear. The buffer layer has covered the entire substrate, and its thickness is greater than a few monolayer (the ion probe depth range). The TOF-MSRI spectrum taken after 30

min does not show a significant difference. It remains also unchanged after the annealing at 750 °C.

3.2 Gas Source MBE

In this technique, we used ammonia gas as the group V nitrogen source and elemental Ga, from a heated effusion cell, for the group III material. Using this method, single crystal GaN thin films with growth rates as high as 7500 Å/hr were obtained. The growth rate and the crystalline quality, as well as the optical and electrical properties of these thin films, were extremely dependent on the Ga/NH₃ flux ratios, the substrate temperature, and the pre-deposition treatment. Below, we will summarize the results in optimizing the above parameters using TOF-MSRI and RHEED in-situ and PL ex-situ.

3.2.1 Substrate Nitridation

Following the sample's introduction into the growth chamber, the substrate surface was exposed to a nitridation step. In GSMBE, the nitridation is performed by exposing the clean sapphire substrate to an ammonia beam. The nitridation process depends on the substrate temperature and the exposure time. Similarly to ECR-MBE growth, TOF low energy ion scattering MSRI and RHEED confirmed the surface nitridation. Using ammonia, the onset of nitridation occurs at a surface temperature of 780 °C. At this temperature, a small nitrogen peak is detected by TOF-MSRI. The nitrogen signal is quite small, when compared to the case of ECR-MBE nitridation. The ammonia nitridation is clearly less effective than energetic N species. The need for thermal dissociation of ammonia requires nitridation at elevated temperatures (>780 °C). Such a high temperature limits the residence times of the reactants, and results in desorption of the N species before the nitridation reaction can occur. Such a reaction also requires an O to N exchange step, which further reduces the nitridation reaction probability when using ammonia. The oxygen peak, as measured by TOF-MSRI, is not significantly changed with nitridation time. This supports the argument that very little O to N exchange has occurred. Furthermore, RHEED images acquired during nitridation show a transition from a 2D-diffraction pattern (from an ordered sapphire surface) to a diffused image—no clear spacing related to an AlN over-layer was observed. These results agree with a previous report claiming that an amorphous phase aluminum oxy-nitride (AlON) layer was observed after ammonia nitridation of sapphire during MOCVD growth. [13]

3.2.2 Buffer Layer

In our experiments, the buffer layers were typically grown by GSMBE at a substrate temperature of 550 °C. An immediate observation was that GaN film deposition occurred below the previously measured ammonia decomposition temperature (780 °C). The availability

of Ga or a GaN surface seems to enhance the reactivity of the ammonia precursor. [14] It is apparent that this GaN layer does not fully cover the substrate since both the Al and O peaks still appear on the spectrum.

RHEED analysis of these GaN buffer layers shows diffuse and very dim patterns such as those from near amorphous and rough surfaces. The buffer layer's crystal ordering and surface morphology improve with annealing temperature. TOF-MSRI data taken during this process show a significant change in the Ga/N ratio (from 5.4/1 to less than 2.5/1). The change in the Ga/N ratio is exclusively due to a decrease in the Ga signal. This is interpreted as desorption of the excess elemental Ga from the low temperature GaN layers. The excess Ga is expected to reduce the crystallinity of the material and, through formation of gallium droplets, significantly increases the surface roughness. The annealing results in a crystalline surface with superior morphology. Low energy electron diffraction (LEED) studies, on amorphous GaN buffer layers grown by MOCVD, have reported that post-growth re-crystallization occurs during annealing. [15]

3.2.3 In-Situ Growth Optimization

Prior to optimizing the growth of thick GaN layers, we first undertook a series of experiments investigating the relationship between the surface stoichiometry and the ammonia and gallium fluxes. Intuitively, one should expect that the more stoichiometric the surface, the better the epitaxy. Our main concern, however, was to determine the initial growth conditions which allow the best Ga/N ratio while keeping the lowest possible flow of corrosive ammonia. TOF-MSRI was utilized to measure in-situ the Ga/N ratio during GaN deposition.

The dotted curve in figure 4 presents data for a substrate temperature at 800 °C and a Ga cell temperature at 950 °C (beam equivalent pressure (BEP) of 2.8×10^{-6} torr). The ammonia pressure is decreased from above 1.0×10^{-4} torr to less than 5.0×10^{-6} torr as measured by a flux gauge in the growth chamber. Under these conditions, we find that the Ga/N ratio increases rapidly for either too high or too low flows. There is, however, a large window where a near unity Ga/N peak intensity ratio can be easily maintained. The increase for low ammonia flows can be easily understood through a simple surface depletion argument. That at high flows is more difficult to interpret. RHEED patterns from these surfaces do not show any obvious transition of surface structure. We hypothesize that the reaction by-product (H_2) should be effectively formed on the surface, and liberated for the completion of GaN synthesis. If the ammonia arrival flux is high, most surface area is occupied by source molecules. Above a certain threshold the number of available H atom adsorption sites becomes

limited, and the NH_3 decomposition rate is reduced. Consequently, the Ga/N ratio increases for very high ammonia pressures

The solid curve in figure 4 also shows results from a similar experiment with the exception that the Ga cell temperature is increased by 50 °C to 1000 °C. Two observations can be made: (i) the low Ga/N window becomes extremely narrow with a minimum Ga/N ratio of 2.5 (at 8.5×10^{-6} torr) and (ii) the Ga/N ratio for most of the pressure range is ~ 5 . The low-pressure side explanation is similar to the previous case. The overall increase in the Ga/N ratio can be explained simply by a larger equilibrium Ga surface population. There is, however, a narrow window where the Ga/N is at a minimum. The ammonia surface dissociation and reaction must be very sensitive to the total surface coverage of source molecules. Too little surface Ga lowers reactivity due to the lack of enough number of Ga atoms for the reaction with NH_3 ; too high Ga fluxes blocks intermediary reaction paths and lowers the incorporation rates.

3.2.4 Correlation between TOF-MSRI and Photoluminescence

To further investigate the extent to which the GaN epilayer's properties depend on the low temperature buffer layer, we designed the following experiment. GaN thin films were deposited on sapphire with GSMBE at fixed growth conditions with the exception that the nitridation and buffer layer steps were different in each case. The final layers were all grown by GSMBE. At the end of each growth, TOF-MSRI was utilized to measure the surface stoichiometry. Figure 5 clearly displays a relationship between the Ga/N ratio, the oxygen impurity level, and the photoluminescence (PL) full width half maximum (FWHM) and intensity.

The closer to stoichiometry the surface, the better the PL result. While at first, a sample (Ga/N = 3.0 but FWHM = 158 meV) may seem to be an exception, a closer analysis of its MSRI spectrum shows a surface oxygen shoulder from either ammonia contamination or improper initial growth conditions. These results are significant for use of TOF-MSRI as a real time optimization tool for GaN materials development and control of optoelectronic device fabrication.

3.3 Chemical Beam Epitaxy

As in GaN metal organic chemical vapor deposition (MOCVD), high vapor pressure organo metallic precursors containing group III metals and hydride group V compounds are normally used for source materials in CBE thin film growth. The group III precursor gas lines were maintained at 35 °C.

3.3.1 Nucleation

Prior to thin film deposition, the substrate was nitridated using the ECR source. To that end, the sapphire sub-

strate, at a temperature of 750 °C, was exposed to the N₂-ECR source for 10–15 minutes.

Initially CBE buffer layer growth was attempted using standard procedures with TEG and NH₃ precursors. No clear GaN nucleation was observed on the surface at any growth temperature. The TOF-MSRI results from these initial studies are described in figure 6. At temperatures below 550 °C, only a weak MSRI Ga peak is observed. In the absence of a nitrogen signal, this indicates that deposition of Ga or coordination of TEG on the surface occurred. When the growth temperature is increased to 750 °C in order to enhance the ammonia surface dissociation, TOF-MSRI measurements again still revealed no GaN deposition. Only a very little nitrogen peak is found with absence of Ga signal. The previously deposited Ga was evaporated and an AlN overlayer was formed during this process. The presence of TOF-MSRI signals from the sapphire substrate (aluminum and oxygen) further indicates that coverage is incomplete under both conditions. The lack of GaN nucleation directly on the nitridated sapphire substrate most likely results due to the following reasons: (i) At these low temperatures the ammonia dissociation is minimal but, as shown in GSMBE, is enhanced by a Ga rich surface. In the case of a surface TEG or the intermediate diethyl gallium (DEG) molecule, such an enhancement might not occur due to a less favorable bonding configuration. (ii) The TEG surface binding energy, being much weaker than Ga, can result in a low overall residence time of the TEG-NH₃ complex. Consequently the TEG-NH₃ complex is less bound to the surface and desorbs. The surface residence time can be made lower if the TEG surface bond gets weaker upon reaction between TEG and NH₃. (iii) Our experimental results show a very high oxygen content in these low temperature buffer layers. Considering that oxygen gets incorporated into the layers from an oxidized Ga precursor (for example, GaR_{3-X}(OR)_X with X=1,2,3), where the gallium is less electron deficient than in TEG since the oxygen from the Ga-O bond provides it with an electron. The oxidized Ga compounds then becomes less bound to the surface and desorbs more readily. In addition, the reaction intermediate, NH₃-GaR_{3-X}(OR)_X, is more difficult to form (higher activation energy is required) than TEG-NH₃.

Due to the difficulty of nucleating a GaN film on sapphire with CBE, we switched the group V nitrogen source from ammonia to ECR plasma activated nitrogen and deposited a low temperature buffer layer with N₂-ECR using TEG as the group III precursor. This method is analogous to metal organic MBE (MOMBE) epitaxial growth. The N₂-ECR plus TEG growths resulted in

GaN films at substrate temperatures as low as 450 °C. The TOF-MSRI spectrum from these thin layers contains Ga and N peaks without any Al signal. The buffer layer is thus continuous and covers the entire substrate. Carbon and oxygen signals are also visible on the same spectrum.

The carbon peak originates from the group III organometallic precursor. Its intensity significantly decreases after a high temperature annealing. The oxygen signal is stable and remains constant. The oxygen incorporation is either due to surface diffusion from bulk or an impurity present during the deposition process. TOF-MSRI from either ECR MBE (Ga+N₂) or GSMBE (Ga+NH₃) GaN thin films grown in the same reactor do not show any residual surface oxygen. Based on this fact, the oxygen most probably originates from the reaction of O₂ with the TEG precursor. The result is a very stable alkoxide intermediate.

The oxygen is thus very efficiently delivered to the growth surface as a C-O bond. The carbon subsequently desorbs upon annealing leaving the oxygen behind. This is consistent as well with the lower strength of the Ga-C bond relative to that of either Ga-N or Ga-O.

3.3.2 The Influence of Carbon Incorporation on Film Quality

Following the initial deposition of crystalline low temperature GaN buffer layers, GaN thin films were deposited with CBE at growth rates from 1000–4000 Å/hr. For CBE growth of the final layers, the substrate temperature was varied from 700–850 °C, and different TEG to ammonia flow ratios were investigated. The substrate temperature and precursors flow rates were varied in an effort to produce crystalline high purity films.

The carbon surface composition was monitored *in-situ* by TOF-MSRI. Our results show that the incorporation of carbon is both temperature and TEG/NH₃ ratio dependent, but clearly, the substrate temperature is the most critical factor controlling crystalline quality. A clear correlation also exists between surface carbon composition and GaN crystallinity. Growths performed at a constant substrate temperature of 850 °C, but with increasing TEG to NH₃ flow ratio, yield thin films with higher surface C content and deteriorating crystalline quality (as determined by RHEED). In this study, we carefully investigated the growth temperature range between 700 °C and 850 °C. Only polycrystalline films were grown below 750 °C, but single crystalline layers were achieved for higher temperatures. At 750 °C, both textured polycrystal and 3D transmission single crystalline RHEED diffraction features were observed. It is only in a narrow temperature window (800–825 °C) that

two-dimensionally (2D) smooth single crystal layers were obtained.

A correlation between surface carbon composition and GaN crystallinity is further supported when growths at a constant substrate temperature of $\sim 850^\circ\text{C}$, but using various TEG to NH_3 flow ratios, yield the same results: as TEG flow (surface carbon) increases, crystallinity deteriorates. RHEED patterns from CBE GaN layers grown at different TEG flow rates showed deterioration of film crystallinity while TEG/ NH_3 flow ratio was increased. Both the surface carbon and hydrogen signal intensities increase with TEG flow.

4 Conclusion

The sapphire substrate nitridation process is clearly determined by TOF-MSRI, which is shown to be more sensitive to onset of nitridation than RHEED. In the case of ECR- N_2 plasma nitridation, the optimum temperature and saturation of N/O peak intensity ratio was observed. ECR- N_2 plasma nitridation is more effective for oxygen replacement than ammonia gas. ECR MBE resulted in continuous crystalline coverage buffer layer while non-crystalline discontinuous buffer layers were grown by GSMBE. In the case of CBE, low temperature nucleation was not observed, so that buffer layers were grown by MOMBE.

Gas source MBE, using ammonia and Ga, was utilized in GaN thin films growth. The chemical decomposition and incorporation of NH_3 in the thin films were studied for different growth conditions. The nitridation of sapphire was demonstrated but was determined to be much more difficult to achieve than with an ECR plasma source. GaN epilayers grown with a low temperature buffer layer exhibited superior film quality. A direct correlation between in-situ TOF-MSRI and ex-situ PL results was observed. Samples with a low Ga/N ratio in TOF-MSRI showed the best optical quality. The NH_3 pressure during growth significantly influenced this Ga/N ratio.

TOF-MSRI identified that nucleation layers could not be deposited directly on the sapphire substrate using the CBE precursors. The use of TEG and ECR- N_2 species allowed the growth of crystalline buffers. The growth temperature and N_2 flow strongly affected the crystallinity of these buffer layers. Amorphous and polycrystalline buffer layers became island-like upon annealing to 900°C in vacuum while the crystalline buffer layers remained unchanged. Similarly, the epilayers' crystal quality depended critically on the growth temperature and TEG flows. TOF-MSRI studies found that the residual carbon level is highly temperature

dependent and influenced greatly the surface morphology and crystallinity (from RHEED). It is only within a narrow temperature window, $800\text{--}825^\circ\text{C}$ that the carbon level is at a minimum. Within that range, GaN epilayers with strong band edge PL signals were obtained. The oxygen surface levels, as measured by TOF-MSRI, in all CBE GaN were high and did not decrease after annealing. It is postulated that an oxidized Ga compound in the TEG source is at the origin of such high levels.

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FIGURES

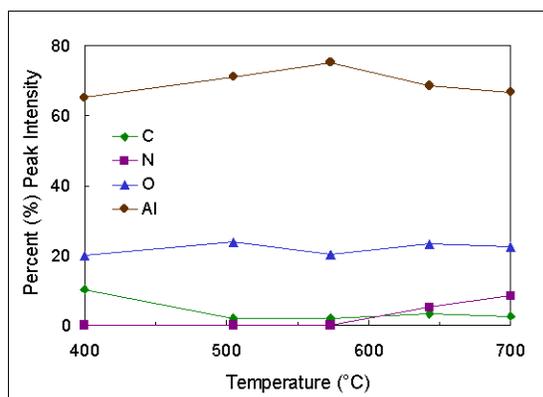


Figure 1. The change of surface elemental population of a sapphire substrate during ECR plasma nitridation. The relative peak intensities are obtained by TOF-MSRI at different surface temperature.

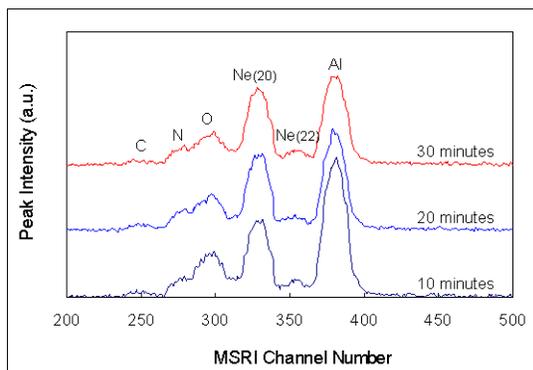


Figure 2. The TOF-MSRI spectra vs. ECR-nitridation exposure time from a sapphire surface. The ECR power is 200 W and the substrate temperature is 700 °C.

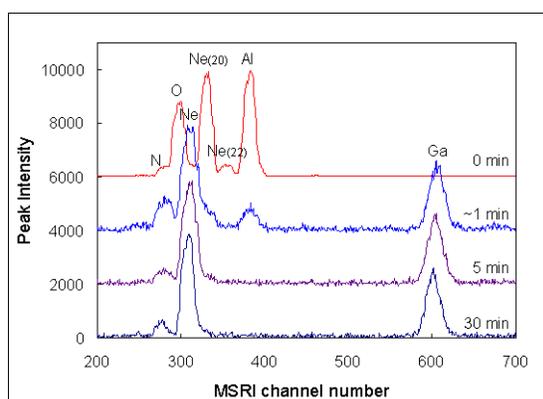


Figure 3. TOF-MSRI spectra during a GaN buffer layer deposition. The neon scatter peak position shifts to lower time of flight due to the ECR plasma operation during the second, third and fourth spectra acquisitions.

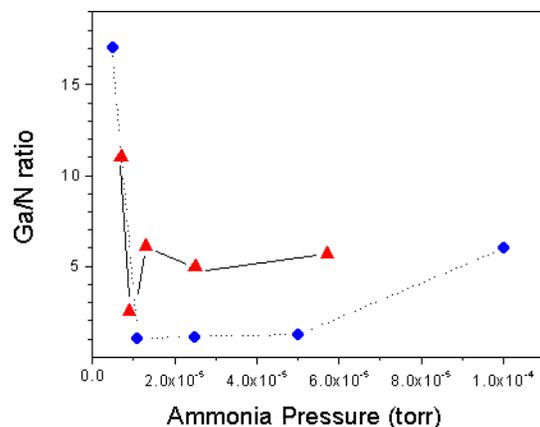


Figure 4. Ga to N peak intensities measured by TOF-MSRI during GSMBE growth of GaN under varying ammonia gas pressure. The dotted curve is obtained for a Ga cell of 950 °C. The solid curve is obtained for a Ga cell of 1000 °C. In both cases, the substrate temperature is 800 °C.

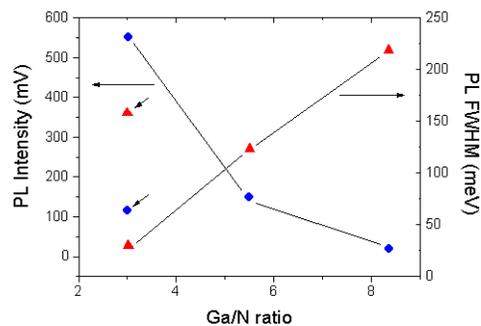


Figure 5. The correlation of optical properties of GSMBE GaN and Ga/N peak intensity ratio as measured by TOF-MSRI. PL band edge peak intensity (red triangles) and FWHM of PL signal (blue circles) at 10 K. A deviation is found for the sample containing oxygen as a contaminant by TOF-MSRI (marked by short arrows).

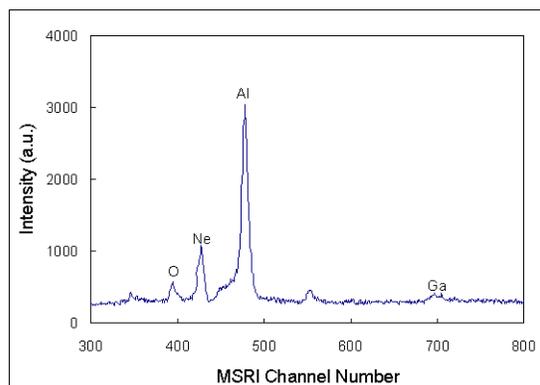


Figure 6. A TOF-MSRI spectrum from a sapphire substrate exposed to NH₃+TEG at 550 °C. Only a small Ga peak is seen in the absence of N peak.