### Report Title
**Improved Gallium Nitride and Aluminum Nitride Electronic Materials**

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### Summary
This report describes the results of a three year program to improve the quality of Group III nitride electronic materials. The effort was directed toward understanding and controlling surface-reactive chemical paths toward the growth of GaN. We demonstrated low temperature synthesis of GaN from trimethyl gallium and ammonia by two techniques: a two-step process using atomic hydrogen and electron beams, and a single step process using only an electron beam. The electron beam activation made it possible to grow GaN in patterns.

Several novel tools for the growth and processing of semiconductor materials resulted from this work. (i) A liquid N2-cooled reflector source of atomic hydrogen was developed for chemical activation and reactive cleaning of semiconductor surfaces. (ii) An electron beam was used to stimulate the GaN synthesis reaction, providing a tool for activation of growth reactions which is an alternative to ion beams. These techniques were particularly effective in removing carbon associated with the methyl radical.

In a parallel effort we carried out cathodoluminescence and infrared reflectance studies of GaN, AlN, superlattices, heterostructures with related wideband materials, providing information on the material defects and structure. We developed a model which allows the extraction of structural information of the component materials from infrared reflectance measurements near the restrahlen region.

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Photograph of the UHV vacuum chamber, analytical tools, and associated electronics used on the study of the synthesis of GaN from alkyl surface reactions.
IMPROVED GALLIUM NITRIDE AND ALUMINUM NITRIDE ELECTRONIC MATERIALS

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ABSTRACT

This report describes the results of a three year program to improve the quality of Group III nitride electronic materials. The effort was directed toward understanding and controlling surface-reactive chemical paths toward the growth of GaN. We demonstrated low temperature synthesis of GaN from tri-methyl gallium and ammonia by two techniques: a two-step processes using atomic hydrogen and electron beams, and a single step process using only an electron beam. The electron beam activation made it possible to grow GaN in patterns.

Several novel tools for the growth and processing of semiconductor materials resulted from this work. (i) A liquid N2-cooled reflector source of atomic hydrogen was developed for chemical activation and reactive cleaning of semiconductor surfaces. (ii) An electron beam was used to stimulate the GaN synthesis reaction, providing a tool for activation of growth reactions which is an alternative to ion beams. These techniques were particularly effective in removing carbon associated with the methyl radical.

In a parallel effort we carried out cathodoluminescence and infrared reflectance studies of GaN, AlN, superlattices, and heterostructures with related wideband materials, providing information on the material defects and structure. We developed a model which allows the extraction of structural information of the component materials from infrared reflectance measurements near the restrahlen region.
1. OVERVIEW

The body of this report consists of an executive summary of the program results, presenting our objectives, results, and conclusions in a manner that is readable by technical individuals that are not necessarily experts in surface science, semiconductor material growth, or characterization. The surface chemistry work is presented in Section 2, and the characterization work is presented in Section 3. It is described in much greater detail in the articles that we have published, or submitted for publication in the scientific literature. We provide references to the articles that are now in print, and we have included copies of key articles not yet in print as appendices to this report.

A complete list of the publications and patent disclosures that were produced on this program is provided in Section 4.

2. SURFACE-CHEMICAL SYNTHESIS OF GaN

The objective of this effort was to develop non-thermal paths to the synthesis and growth of Group III nitrides. We concentrated on the reaction of trimethyl gallium: \( \text{Ga(CH}_3)_3 \) with ammonia: \( \text{NH}_3 \). It is important to use non-thermal synthesis routes with GaN because of its chemical instability at high temperatures\(^1\). The high equilibrium vapor pressure of nitrogen over hot GaN makes conventional melt or solution growth impossible at pressures below about 15 kbar. The presence of ammonia in the vapor improves the situation considerably\(^2\), but it is widely believed that the nitrogen instability leads to a high level of defects in thermally activated growth of GaN. Super-reactive species, such as nitrogen ions have been provided at the GaN growth surfaces to counteract this effect\(^3,4,5\), and promising results using these approaches have been reported.

As an alternative to these, our approach uses highly reactive atomic hydrogen and electron beams to activate the reaction, specifically excluding ion beams. We believe that our approach has the potential for less collisional disturbance of the growing surface because of the low mass of the electrons (a
3 keV electron has about an order of magnitude less momentum than a 10 eV nitrogen ion). The techniques developed here proved to be extremely effective in removing the carbon that is associated with the methyl radicals of the trimethyl gallium.

By carrying out our experiments at low temperatures in the 100 K range, we have been able to characterize the process kinetics, providing a high degree of understanding that cannot be obtained by other techniques. This includes obtaining the parameters necessary for predicting the process characteristics at more practical growth temperatures in the 900K range, high enough to obtain the surface mobilities needed for good epitaxial growth, but low enough to avoid loss of nitrogen.

The following subsections contain descriptions of the experimental apparatus and methods, the description and characterization of the cooled, low-energy atomic hydrogen source developed on the program, and a discussion of the key experiments in which we removed the methyl radicals from adsorbed layers of trimethyl gallium and converted the resulting layers to GaN.

2.1. Experimental Apparatus

A schematic of the experimental apparatus developed and used for this work is shown in Fig. 2.1. It contains:

a. A multicapillary array molecular doser which provides a calibrated beam of collimated molecules to the surface. It is equipped with a shutter for kinetic uptake measurements;

b. A quadrupole mass spectrometer for collecting species desorbed from the surface. It is housed in a differentially pumped shield, with an aperture that admits gas desorbed from the central region of the sample, discriminating against desorption from extraneous locations. It is equipped with a bias shield to prevent escape of the electrons from the ion source;

c. An Auger electron spectrometer for surface analysis, and for providing an electron beam for stimulating surface reactions;
d. A reverse view LEED apparatus for structural characterization;

e. A cryogenically cooled reflector source of atomic hydrogen, which is
provides a low energy beam of H without the high radiant flux that usually
accompanies filament-dissociated H sources.

Fig. 2.1 Schematic of the UHV surface chemistry apparatus at the University of
Pittsburgh used for the study of synthesis of GaN from alkyls.

The steel UHV system is pumped by a 270 l/s in pump, a 150 l/s turbo pump,
and a titanium sublimation pump. It achieves a base pressure of 5X10⁻¹¹ Torr.
This apparatus provides the capability for control and characterization of
surface synthesis reactions by introducing known fluxes of neutral species to
the sample surface, measuring the kinetics of the adsorption of these species
on the surface, measuring surface kinetics by mass spectroscopy of desorbed
species, introducing reactive H and electron beams to activate chemical reactions, and monitoring the composition and character of the surface species to determine the results of the reactions. A photograph of the apparatus is shown as the frontispiece of this report.

2.2. Reflective Atomic Hydrogen Source

This tool was invented on the program to solve the problems caused by excessive sample heating from the hot tungsten filament used to dissociate molecular hydrogen into atomic hydrogen. It takes advantage of the fact that the reflectivity of a cooled Pyrex glass surface is high for atomic hydrogen, but low for optical and infrared radiation, the main mechanism of sample heating. The recombination of atomic H on Pyrex has been reported to be in the range of $10^{-3}$ to $10^{-4}$, while the reflectance of optical and near infrared radiation from the first surface is about 4%. The Pyrex was cooled to about 120 K to avoid possible evolution of impurities due to the incident atomic H. A schematic diagram of the source is shown in Fig. 2.2. It consists of a flat spiral tungsten filament located at that exit of a stainless steel effusive dosing arrangement, shielded from direct line-of-sight exposure to the sample.

![Fig. 2.2 Schematic diagram of the reflector atomic hydrogen source.](image)
We calibrated the source by using a Si(100) crystal surface as a collector, employing temperature programmed desorption of H₂ to measure the amount of atomic H received by the crystal. The temperature dependence of the atomic H production rate as a function of temperature is shown in Fig. 2.3. The data show that above a filament temperature of about 2000 K, the production rate of H reaches a plateau, in agreement with the results of Koehler et. al. We therefore selected a filament temperature of 1800 K for our experiments, producing a reproducible rate of atomic H generation.

Fig. 2.3 Efficiency of atomic hydrogen production on the tungsten filament of the cooled atomic hydrogen source.

A photograph of the prototype of the atomic H source is shown in Fig. 2.4, showing it rugged and practical construction, and compatibility with standard
UHV systems. We believe that the cool, clean atomic H beams produced by this source would be useful for many applications for surface cleaning where surface damage, heating, and impurities must be minimized.

Fig. 2.4. Photograph of the prototype cooled reflector-atomic H source used in this work.

2.3. Decomposition of Ga(CH₃)₃-Derived Layers By Atomic H

We used atomic H from our cooled reflector source to deplete the carbon from layers produced by adsorption of Ga(CH₃)₃ on SiO₂ surfaces⁹. It is known¹⁰ that Ga(CH₃)₃ partially dissociates on SiO₂ surfaces to form Ga(CH₃)₂, so we designate this first layer as Ga(CH₃)ₓ. The dissociation is postulated to occur on the surface Si-O-Si groups. Using temperature programmed desorption, we have observed that from this monolayer, Ga(CH₃)₂ (m/e = 99) desorbs at its maximum rate at 155 K, as shown on the bottom desorption spectrum of Fig 2.5. For this monolayer coverage, almost no Ga(CH₃)₃ (m/e = 114) is seen to desorb.
Fig. 2.5. Depletion of m/e = 99 thermal desorption product following various atomic H exposures at 108 K. Complete loss of this product is observed for approximately 100 monolayers of atomic H exposure.

Upon exposing the surface at 108 K to various doses of atomic H, it is evident that the Ga(CH₃)ₓ is depleted from the surface, and after about 100-200 monolayers of atomic H exposure it is completely removed. This conclusion is substantiated by the similar behavior seen in the Ga⁺ fragment (m/e = 69), as shown in Fig. 2.6. Subsequent Auger spectroscopy measurements indicate that after exposure of the surface with atomic hydrogen, elemental Ga remains
up to temperatures of 800 K. These results show that atomic H activates a major modification of the layers derived from Ga(CH₃)₃ adsorption, and the final product appears to be devoid of C. The kinetic experiments described in the following section show that this is indeed the case.

Fig. 2.6. Depletion of the m/e = 69 thermal desorption product following various atomic H exposures at 108 K. Complete loss of this product is observed for approximately 100 monolayers of atomic H exposure.
2.4. Kinetics of Extraction of CH\textsubscript{3} by Atomic H

Three experiments to examine the kinetics of CH\textsubscript{3} extraction by atomic H were performed in the temperature range of 97 K to 138 K. Auger spectroscopy was employed to monitor both the C(KLL) and the Ga(LMM) intensities following various exposures to atomic H. Each measurement was made after moving the crystal so that a fresh region of the crystal was exposed. The left hand side of Fig. 2.7 shows the Auger measurements. It is seen that the C is depleted efficiently by atomic H exposure, and to within experimental error, it is totally depleted after about 100 monolayers exposure of atomic H, in agreement with the measurements described above.

The behavior of the Ga (LMM) Auger signal during exposure to atomic H is also consistent. Initially, a slight decrease in the Ga(LMM) signal is observed. This is followed by an overall increase as the CH\textsubscript{3} groups are removed. The slow increase in Ga(LMM) is due to a reduction of the screening of primary and Auger electrons, as expected from the reduction in the surface coverage of CH\textsubscript{3} groups.

The right hand side of Fig. 4 presents the C(KLL) Auger intensity in a semilog plot as a function of exposure to atomic H. The linear behavior observed is indicative of a CH\textsubscript{3}-extraction reaction which is first order in the surface coverage of CH\textsubscript{3} groups. The slope of the first order plots is independent of substrate temperature over the 41 K range investigated. From these slopes, and estimated errors, an activation energy for the H-induced extraction process is determined to be 0 (+0.09, -0.02) kcal/mole.
Fig. 2.7 Kinetics of extraction of CH$_3$ by atomic H from one monolayer of Ga(CH$_3$)$_x$ on SiO$_2$/Si(100) at three temperatures. The behavior of both the C(KLL) and the Ga(LMM) Auger intensities are shown on the left. On the right, semilog plots of the c(KLL) Auger signals are shown.
2.5. Electron Beam Conversion of H-Stripped Layers to GaN

We demonstrated the synthesis of GaN monolayers from the Ga(CH$_3$)$_3$-derived layers that had been stripped of carbon with atomic H. The chamber was backfilled with NH$_3$ to produce a steady state coverage of NH$_3$ on the surface. Since metallic Ga does not react with NH$_3$ at our sample temperatures, the nitriding reaction must be activated, and we selected an electron beam for this purpose. The central portion of the sample was exposed to electron bombardment with the electron beam from the Auger spectrometer, and a dot of GaN was produced in this location. This was verified by the shape of the Auger N(KLL) signal (which will be discussed later in this section), and by the thermal desorption characteristics: the dot did not change significantly upon heating to 900K, while the unreacted region around the dot essentially vanished. The entire process is summarized in Fig. 2.8. This demonstration proved the basic feasibility of the process for producing GaN, but the process is complicated, and difficult to envision as a practical growth technique. In the following sections, we describe a much more practical process in which the carbon stripping and the nitridation is done in one step with an electron beam.
Fig. 2.8, Schematic representation of the two-step process for forming monolayers of GaN.
2.6. Electron-Induced Reactions of NH₃ With Ga(CHₓ)

Building on the demonstrated ability of atomic H to break the Ga-CH₃ bond, we carried out experiments\textsuperscript{11} in which the source of atomic H was the electron bombardment of adsorbed NH₃ in the presence of an adsorbed monolayer of Ga(CH₃)x. This was done by backfilling the vacuum chamber with NH₃ immediately following adsorption of Ga(CH₃)₃ on a SiO₂ surface, and subjecting the mixed layer to the electron beam. The results of the experiment for three NH₃ pressures is shown in Fig. 2.9. On the left side of the figure, the decrease in the C(KLL) Auger intensity, compared to control experiments with no NH₃, is shown for increasing exposure to electrons. The rate of CH₃ removal increases monotonically with the pressure of NH₃, and hence the coverage of NH₃ and with the supply of atomic H produced from the adsorbed NH₃. Linear semilogarithmic plots, shown in the right side of Fig. 2.9, indicate that the kinetics of removal of CH₃ groups are first order in the surface coverage of CH₃ groups. A cross section, QPNH₃, for the removal process, was determined from these plots. As expected, it was observed to increase for increasing ammonia pressure, PNH₃, which increased the NH₃ coverage.
Fig. 2.9. Electron-induced reaction of NH₃ with Ga(CH₃)ₓ/SiO₂. Shown is the C(KLL) Auger signal (left side) and its normalized natural logarithm (right side) versus the number of electrons per cm².
Confirming that the CH$_3$ groups were being preferentially removed from the Ga(CH$_3$)$_x$ monolayer by the use of atomic H produced from adsorbed NH$_3$, Fig. 2.10 shows the behavior of the Ga(LMM) Auger intensity for the same experiment that is shown in Fig. 2.9. On the left side of Fig. 2.10, the Ga(LMM) intensity is plotted versus the fluence of electrons. A semilogarithmic plot of the Ga behavior is shown on the right side. It is seen that within experimental errors, the small rate of loss of Ga(LMM) intensity in the electron beam does not change when the NH$_3$ pressure is raised to 5 x 10$^{-8}$ Torr. A comparison of the rate of carbon loss and the rate of Ga loss (Figs. 2.9 and 2.10) for the same pressure of NH$_3$ shows that the rate of loss of carbon is comparatively high as a result of the interaction of the electron beam in the presence of adsorbed NH$_3$. Control experiments in a background of N$_2$, monitoring both C and Ga, indicated that no measurable depletion effect exists as a result of the presence of N$_2$. Thus the CH$_3$ removal process, using electron beam excitation, is correlated with the presence of species containing hydrogen, namely, NH$_3$. 

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Fig. 2.10. The Ga(LMM) Auger signal (left side) and its normalized natural logarithm (right side) versus the number of electrons per cm$^2$ for the electron-induced reaction of NH$_3$ with Ga(CH$_3$)$_x$/SiO$_2$. 
2.7. Direct Formation of GaN Patterns with an Electron Beam

Utilizing the capability of the electron beam to both strip the carbon and activate the nitridation we produced GaN dots in a single step process as shown schematically in Fig. 2.11. The reaction described in the Sect. 2.6 was carried out in a localized region in the center of the substrate, producing GaN in the area exposed to the beam. As before, we found that heating the sample to 900 K resulted in removal of the species from the non-irradiated regions, and the stable GaN remained.

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Fig. 2.11. Schematic diagram of the mechanisms for GaN production by an electron-induced reaction of adsorbed Ga(CH$_3$)$_3$ with NH$_3$ at 108 K.
The data supporting this picture are shown in Fig. 2.12. The left side shows three schematics of the layer structure at key points in the process, while the right side shows that Auger spectra for each. The top row shows the Auger spectrum of the adsorbed Ga(CH₃)ₓ. Following electron exposure in ambient NH₃, the second row shows that C has been removed, only N and Ga signals are seen. Upon heating to 300 K, the lower spectra show that the N and Ga signals are unchanged in the irradiated area, but are greatly reduced elsewhere, indicating that the stable GaN produced in the center is unaffected, but the volatile unreacted species have desorbed.

Fig. 2.12. Monolayer GaN synthesis on SiO₂ by an electron-induced reaction of Ga(CH₃)ₓ with NH₃ at 108 K.
We repeated the procedure shown in Fig 2.11 a second time to grow another layer of GaN on the dot. We see in Fig 2.13 that almost complete removal of carbon has been achieved by the electron beam + NH₃ treatment, and prominent N and Ga features are observed to remain in the irradiated region following heating to 900 K. By this temperature, even smaller residual signals are seen on the non-irradiated regions.

Fig. 2.13. Multilayer GaN synthesis on SiO₂ by an electron-induced reaction of adsorbed Ga(CH₃)₃ with NH₃ at 108 K.
2.8. N(KLL) Auger Lineshape for Electron Beam-Produced GaN

The N(KLL) Auger feature of the GaN dot, both for monolayer and multilayer preparation, is shown in Fig. 2.14, along with the Auger line from a thick layer of GaN and from a thick layer of Si₃N₄. For a film of GaN produced at the one monolayer level, both GaN and Si₃N₄ will be observed by Auger spectroscopy, since Si₃N₄ is also made by the electron beam on the SiO₂ substrate. With increasing thickness of the GaN film, the N(KLL) Auger lineshape will approach that of GaN, but as long as the thickness of the GaN film is of the order of the escape depth of the Auger electrons, about 10Å, there will be a contribution from the underlying Si₃N₄ also, as seen in Fig. 2.14. This may contribute to the lack of exact agreement in the N(KLL) Auger lineshape with that measured for the GaN standard. The data of Fig. 2.14 indicate that the multilayer Auger line shape more closely agrees with the lineshape for bulk GaN than does the monolayer GaN lineshape (as expected).

Fig. 2.14. Normalized and superimposed lineshapes of the N(KLL) Auger signal with increasing thickness of the GaN film. Comparisons to reference thick films of GaN and Si₃N₄ are given.
2.9. Growth of a GaN Line with the Electron Beam

The procedure to produce a dot of GaN was modified to produce a line, and the Auger profile perpendicular to the line was acquired as shown in Fig. 2.15. It was grown at 108 K without subsequent heating, so that both Ga(CH$_3$)$_x$ and NH$_3$ remained adsorbed outside of the line. The C(KLL) Auger signal is seen to be small on the GaN line, but high off the line, while the N(KLL) Auger signal shows the opposite behavior. The data are arbitrarily fitted to a Gaussian profile for smoothing, but it is not the actual functional dependence.

![Profile](image)

Fig. 2.15. Profiles of C(KLL) and N(KLL) Auger signals taken across a GaN line grown by electron beam reaction of NH$_3$ with Ga(CH$_3$)$_x$/SiO$_2$.
2.10. Discussion

2.10.1. Mechanism of Ga-CH3 Bond Breaking by Atomic Hydrogen

As this experimental work was being carried out, a theoretical understanding of the interaction of atomic hydrogen with metal alkyls was achieved by Hiraoka and Mashita, using ab-initio methods\textsuperscript{12}. Their study was directed toward the understanding of the reaction of atomic H with Al(CH\textsubscript{3})\textsubscript{3}, and they employed the H\textsubscript{2}Al(CH\textsubscript{3}) molecule as a model for the trimethylaluminum. Fig. 2.16 illustrates important facts about the attack of atomic H on the Al-CH\textsubscript{3} bond, as deduced by the ab-initio calculations. A hydrogen atom attacks the Al center in the H\textsubscript{2}Al(CH\textsubscript{3}) molecule, producing a stable H\textsubscript{3}Al(CH\textsubscript{3}) intermediate species, with an energy of -3.0 kcal/mol compared to the reactants. This local minimum energy state can then undergo two reactions. Reaction channel a leads to the dissociation of the Al-C bond, producing a CH\textsubscript{3} radical which leaves. The activation energy for reaction a is only 1.9 kcal/mole. An alternate chemical route is the production of a transition complex via reaction channel b. Here the hydrogen atom inserts into the Al-C bond, also causing the bond to break, and producing a CH\textsubscript{4} molecule. The activation energy for this process is calculated to be 12.7 kcal/mole. This overall reaction is exothermic by 21.7 kcal/mole.
Fig 2.16. Atomic hydrogen activation of an aluminum alkyl from ab-initio calculations.

It is likely that similar reactions exist for Ga(CH₃)ₓ species when interaction with atomic hydrogen occurs. From our measurements, it is not possible to determine whether reaction channel a or b is most favored, but both of them involve the scission of the metal-carbon bond and the loss of carbon, either as CH₃ or as CH₄. Further support for the attack of atomic H on the metal atom can be found in recent studies¹³ by Downs et al., where, under hydrogenation conditions, Ga(CH₃)₃ is converted to a digallium molecule containing two bridging hydrogen atoms as shown in Fig. 2.17. This molecule, whose structure has been determined by electron diffraction, represents the first definitive structural characterization of a compound containing two Ga atoms linked by a hydrogen bridge. The digallium molecule is stable to 290 K. The ab-initio
calculations and the structural verification of the replacement of a Ga-CH₃ bond by a bridging H atom leaves little doubt that similar chemistry may be achieved by the exposure of surface species containing Ga-CH₃ bonds to atomic H, as demonstrated in the research reported here. In both cases, attack of the metal atom by atomic H occurs with the elimination of the Ga-CH₃ bond. The low activation energy calculated for the CH₃ elimination compared to CH₄ elimination, in the case of the aluminum compound, may indicate that CH₃ elimination is the favorable kinetic route for the Ga-CH₃ system.

Hydrogenation of Ga(\(\text{CH}_3\))₃

\[
\begin{array}{c}
\text{Ga} \\
\text{CH₃ CH₃}
\end{array}
\quad \text{H} \quad
\begin{array}{c}
\text{Ga} \\
\text{CH₃ H}
\end{array}
\]

\[
\begin{array}{c}
\text{Ga} \\
\text{CH₃ CH₃}
\end{array}
\]


Fig. 2.17. Reaction scheme leading to the displacement of CH₃ groups from Ga(CH₃)₃ under hydrogenation conditions.
2.10.2. Relationship to MOCVD Production of III-V Compounds

This new reaction, involving H atom insertion into Ga-CH₃ bonds, could be very important in MOCVD of MBE processes in which atomic H is present. The reaction can occur both in the gas phase and on the growing film surface, and probably applies to all of the Group III metal alkyls containing CH₃, C₂H₅, etc. alkyl groups. Although our studies were carried out at about 100 K in order to be able to retain high coverages of Ga(CH₃)ₓ on the substrate for investigation, the findings apply directly to deposition processes carried out at higher temperatures, where high surface coverage is provided by high equilibrium pressures of the of the reactants in the case of CVD, or by beams in the case of MBE.

2.10.3. The Electron-Induced Reaction of NH₃ with Ga(CH₃)ₓ/SiO₂

The ability of electron impact dissociation to produce H atoms from the NH₃ molecule was employed as a method of producing a GaN film in the region irradiated by the electron beam. Assuming first-order kinetics for the electron impact induced reaction, the cross section for carbon depletion Q_PNH₃, was evaluated from the slopes of Fig. 2.9, according to the general equation:

\[ N_C = N_C^0 \exp[-(j/e)Q_PNH₃]. \] (1)

Here \( N_C \) and \( N_C^0 \) are the coverage of carbon atoms at time \( t \) and at time 0, respectively, \( j \) is the electron current density, and \( e \) is the elementary charge. The cross section, \( Q_PNH₃ \), is dependent on the pressure of NH₃ because of the dependence of the rate of electron-induced reaction on the steady state coverage of NH₃ achieved under dynamic conditions. The cross section \( Q_PNH₃ \) for depletion of carbon is of the order of \( 5 \times 10^{-20} \) cm² at \( P_{NH₃} = 5 \times 10^{-8} \) Torr.

Under the conditions of this experiment, each electron has an efficiency of order \( 5 \times 10^{-6} \) for causing a CH₃ extraction process⁹. This is due to two inefficient processes working in series:

\[ NH₃ + e^- \rightarrow NH_x + H \] (2)
\[ H + \text{Ga(CH}_3\text{)}_x \rightarrow \text{HGa(CH}_3\text{)}_{x-1} + \text{CH}_3 \text{ or CH}_4 \quad (3) \]

If \( e_1 \) is the efficiency to produce one H per electron in reaction (2), and \( e_2 \) is the efficiency of \( \text{CH}_3 \) extraction by the atomic H thus produced, as described by reaction (2), then the overall process efficiency is \( e_1 \times e_2 \), which we know to be about \( 5 \times 10^{-6} \). We know from Sect. 2.6 that \( e_2 \) is about \( 10^{-2} \), so we can determine that \( e_1 \) is about \( 5 \times 10^{-4} \). This corresponds to an electron impact dissociation cross section of order \( 5 \times 10^{-19} \text{ cm}^{-1} \) for breaking the N-H bond in adsorbed \( \text{NH}_3 \) by electron impact with \( 3 \text{ kV} \) electrons, assuming a steady state coverage of \( \text{NH}_3 \) to be about \( 10^{15}/\text{cm}^2 \).

2.10.4. Growth of GaN

To summarize, the experiments described in this report indicate that GaN can be grown using electron impact of \( \text{NH}_3 \) to produce atomic H, which then reacts with Ga-CH\(_3\) moieties, displacing the CH\(_3\) group. The production of GaN was substantiated by the following experimental results:

a. Carbon is removed by the action of the H atoms produced by electron bombardment.

b. Gallium and nitrogen are thermally fixed in the dot or line which has been subjected to the electron-stimulated reaction conditions.

c. Gallium and nitrogen are not thermally fixed outside of the irradiated area, where reaction conditions are not provided.

d. The GaN produced is thermally stable to 900K.

e. The N(KLL) Auger line shape can be explained by the production of a GaN layer over a Si\(_3\)N\(_4\) layer, which is also produced on the SiO\(_2\)-coated substrate.
2.10.5. Conclusions

The following conclusions can be reached from this work:

a. The reaction between the Ga-CH$_3$ bond and atomic H occurs near 100 K with the elimination of carbon either as CH$_3$ and/or CH$_4$. This process occurs with zero activation energy in accordance with theoretical expectations.

b. The efficiency of the reaction per incident H atom is of the order of 10$^{-2}$. The CH$_3$ extraction is first order in CH$_3$ coverage on the surface.

c. Using an electron beam, incident on adsorbed NH$_3$, atomic H may be generated in the irradiated region of the surface. This atomic hydrogen may also be used to activate the Ga-CH$_3$ bond and GaN may be then produced.

d. This new synthesis method offers the possibility of achieving low temperature growth of GaN films on suitably matched substrates, thus reducing nitrogen vacancies that result from its thermal instability. This technique may result in less carbon contamination from growth from alkyl precursors, and the ability to grow in patterns defined by an electron beam may find novel applications.

e. These findings are very likely to apply in a general way to the production of III-V compound semiconductor films from Group III metal alkyls and group V hydrides.

2.10.6. Acknowledgements

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3. CHARACTERIZATION OF GROUP III NITRIDES

Materials characterization experiments consisted of cathodoluminescence (CL) measurements which provided information on the electronic properties of Group III nitride layers, and infrared reflectance measurements which provided insight into their structural properties\textsuperscript{14}. We collaborated with nine laboratories around the world, providing important material data feedback to both growth groups and device groups.

Significant features near the band edge, which have strong dependence on the character and the purity of the materials, are easily measured by CL. Fig 3.1 shows the spectrum of a GaN film deposited on a sapphire substrate with a GaN buffer layer, in which three sharp free exciton (FE) peaks were identified in a cryogenic CL measurement. Dopants and impurities can be detected and identified by CL. Fig 3.2 shows a peak associated with silicon in a doped GaN film grown on SiC.

![Graph](image)

Fig. 3.1. Cathodoluminescence of a 4.48 μm thick GaN film deposited on a sapphire substrate with a GaN buffer layer.
Fig. 3.2. Cathodoluminescence of a 0.5 μm thick GaN film doped with silicon, deposited on a (0001) 6H SiC substrate.

We developed a Lorentz oscillator model\textsuperscript{15} of the infrared reflectance of AlN layers on substrates such as SiC and Si. The model takes into account film and substrate anisotropy and non-normal incidence rays, and requires only bulk material parameters. Comparison of infrared reflectance measurements to the model provides information on the thickness, orientation, and quality of epitaxial AlN films. As an example, Fig. 3.3 shows the IR reflectance of a GaN film on a sapphire substrate, along with the spectrum predicted by the model. Comparison to the model made it possible to identify the vibrational modes that give rise to the spectral features.
Fig. 3.3. Reflectance of a 4.52 µm thick GaN film on a sapphire substrate. The solid line represents the data, and the dashed line is the calculated spectrum.
4. PUBLICATIONS AND PATENT DISCLOSURES

4.1. Refereed Journal Articles and Proceedings


4.2. Presentations at Conferences


4.3. Patent Disclosures


5. REFERENCES


6. APPENDIX 1:

Ga-CH$_3$ Bond Scission by Atomic H-
The Depletion of Surface Carbon From a Gallium Alkyl
Film on Silicon Dioxide


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Ga-CH₃ Bond Scission by Atomic H-
The Depletion of Surface Carbon From a Gallium Alkyl
Film on Silicon Dioxide


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Abstract

It is shown that atomic hydrogen is an effective reagent for the extraction of
CH₃ groups from an adsorbed monolayer produced from trimethylgallium
adsorption on SiO₂. The reaction is first-order in CH₃ surface concentration and
proceeds with zero activation energy in the 100 K temperature region. The
efficiency for the extraction process is about 10⁻² per atomic H collision with the
surface. These results show that the Ga-CH₃ bond may be broken by insertion of
hydrogen atoms and that either CH₃ or CH₄ is eliminated by the process. The
results indicate that atomic hydrogen is an effective agent for removal of carbon
(present as CH₃) during III-V film growth processes. The extraction of CH₃ by
atomic H occurs on the surface, but in MOCVD processes a similar reaction with
metal alkyl species may also occur in the gas phase. Excellent agreement with the
theoretical calculations of Hiraoka and Mashita for the interaction of atomic H
with AlH₂(CH₃) molecules is found.
1. Introduction

The III-V compounds, in particular the wide band gap nitrides, are very attractive semiconductors for light emission applications in the blue and UV wavelengths at high temperatures [1]. The effort to produce high quality films of III-V compounds can be traced back to the 1960's where much work was initiated in an attempt to better understand compounds such as GaN, InN, and AlN. The earliest GaN samples studied were in the form of powder samples or small crystals [2]. The most prevalent technique for growing these samples was to place metallic Ga in a zone furnace and to flow NH\textsubscript{3} over it [2] or to use a gallium phosphide or gallium arsenide [3a] or a gallium subchloride [3b] source for transport of Ga into the furnace. Another common growth technique was the use of reactive sputtering. This method employed Ar ions to sputter a Ga film in the presence of a nitrogen plasma [4]. The GaN produced by these methods was suitable to investigate and characterize many of its properties; however, material good enough for electronic applications was still elusive. Heteroepitaxial growth was finally realized by the use of CVD (chemical vapor deposition) techniques [1]. This permitted the production of high quality films where the principal problems dealt with finding suitable substrates for a good lattice match, elimination of very high background n-type carrier concentrations thought to be due to nitrogen vacancies, and the incorporation of dopants. The problem of a proper substrate lattice match that is also thermally compatible with the GaN thin film is being investigated by the use of substrate materials such as SiC, ZnO, and MgO [1]. The production of stoichiometric GaN is still a major obstacle for producing electronic grade films. Lower growth temperatures that might allow better nitrogen incorporation from more reactive nitrogen-containing precursors are being considered [5].
The growth of these nitrides, in thin film form using MOCVD (metal organic chemical vapor deposition) and MBE (molecular beam epitaxy), is now widespread and many variations of these two techniques are in use and are just beginning to be understood. In particular the thermal decomposition of trimethylgallium, Ga(CH₃)₃, (TMG) [6], in the presence of NH₃ can be used for GaN film production. This type of process is known to leave carbon behind [7-10] which can be deleterious to III-V semiconductor films.

The use of incoming hydrogen atoms from the gas phase to extract certain absorbates has been experimentally demonstrated to be effective on both semiconductor [11-13] and metal surfaces [14-18]. In many cases this H atom induced extraction process is thought to occur by an Eley-Rideal mechanism where energy accommodation between the incoming H atom and the surface does not occur. We show that atomic hydrogen, (containing 52 kcal/g atom of internal energy compared to 1/2 mole of H₂), is an effective reagent for CH₃ abstraction from the Ga-CH₃ moiety at low temperatures, and that the process occurs without thermal activation. It is possible that either CH₃ radicals or that CH₄(g) is the product in this hydrogen atom abstraction reaction. This reaction may serve as a basis for reducing carbon contamination of GaN (and other III-V semiconductor films) made by MOCVD methods [19].

II. Experimental

The experiments were performed in a stainless steel ultrahigh vacuum (UHV) chamber pumped by a 150 l/s turbo pump, a 270 l/s diode ion pump and a titanium sublimation pump. The base pressure attained was 1 x 10⁻¹⁰ Torr. The chamber is equipped with a differentially pumped UTI-100C quadrupole mass spectrometer (QMS) having an axially oriented aperture of 4.7 mm diameter. The
aperture is biased at -125 V to retard emission of stray electrons from the QMS ion source. This instrument may be employed in two modes of operation. They are: (1) for residual gas analysis, a large aperture on the side of the cylindrical shield surrounding the QMS may be opened to the ultrahigh vacuum system; (2) for temperature programmed desorption (TPD) measurements the aperture is reproducibly located 0.2 mm from the front of the substrate containing the adsorbed layer, collecting a large fraction of the desorbing gas from the central region of the substrate [20]. The vacuum system also contains a single pass CMA Auger spectrometer which was operated with a 0.3 mm diameter electron beam (3 kV, 3.0 μA), a reverse view LEED apparatus and a multicapillary array doser system for deposition of TMG at a known absorbate flux [20-21]. A unique source of atomic hydrogen was employed in this work [22]. Hydrogen molecules are directed in an effusive beam to a pancake spiral W filament at 1800 K, housed in a cylindrical metal radiation shield. The local pressure of H₂ at the W filament is ~50 times higher than the pressure due to the random flux of H₂ inside the chamber from the admitted H₂, producing a large yield of atomic H. A portion of this atomic H exits from the end of the shield and is efficiently reflected from a pyrex glass plate at ~77 K. A fraction of the reflected atomic H flux is incident on the substrate. This indirect method for delivering atomic H to the surface eliminates almost all radiation heating of the substrate.

The rate of adsorption of atomic H on a Si(100) substrate at 600 K may be employed as a method to estimate the rate of impingement of atomic H on the surface [22-24]. Figure 1 shows the rate of buildup of hydrogen coverage on Si(100)-(2x1) maintained at 600 K following exposure to atomic H. The desorbing H₂ from the Si(100) surface is measured by TPD [23]. It is observed that the hydrogen coverage rises almost linearly to a break point, indicating adsorption by a process involving a constant sticking coefficient, S_H. For
purposes of calibration, we assume in this region of coverage that $S_H = 1$, and that at the saturation point, a saturated monohydride surface phase ($6.8 \times 10^{14} \text{ H/cm}^2 = 1 \text{ monolayer (ML)}$) has been produced [23-24]. This saturation point corresponds to a value of the pressure of H$_2$ multiplied by time and is equal to $2.0 \times 10^{-5}$ Torr sec (corrected Bayard-Alpert gauge pressure sensitivity factor = 0.5 for H$_2$ [25]). In this case, the pressure of H$_2$ is a measure of the system pressure during dosing, not the true local pressure of hydrogen at the spiral filament which is ~ 50 times greater. The number of H$_2$ molecules which have entered the H atom doser is given on the abscissa of Fig. 1. Within this framework the value of $2.0 \times 10^{-5}$ Torr sec is proportional to the atomic H exposure on the surface, such that $6.8 \times 10^{14} \text{ H/cm}^2 = 1 \text{ ML} = 2.0 \times 10^{-5}$ Torr sec. All atomic hydrogen doses in the experiments described here are referenced to this 1 ML definition, using the background system pressure of H$_2$ as an index of the flux of atomic hydrogen; this definition of 1 ML H exposure is a definition useful as only a qualitative index of hydrogen atom exposure, since $S_H$ has been assumed to be unity in the estimate, and the location of the monolayer saturation point is somewhat arbitrary.

The substrate used for this study was a SiO$_2$ film grown on top of a clean Si(100) crystal (13 x 13 x 1.5 mm$^3$; p-type; B-doped; 10 ohm/cm). The crystal containing the SiO$_2$ film may be cooled to ~ 95 K using liquid N$_2$. A temperature controller, working with a feedback thermocouple signal, allows programmed heating of the Si(100) crystal from 95 K to 1200 K [26]. The chromel-alumel (Type E) thermocouple is embedded in a slot in the edge of the Si(100) crystal, and protected from touching the inner Si surface by a double envelope of Ta foil [21]. Growth of the SiO$_2$ film was done by using the sputter-oxidation procedure of Chen et al. [27]. This was achieved by back filling the chamber with $2.0 \times 10^{-5}$ Torr oxygen and using the argon ion sputter gun (with direct Ar admission to the gun) giving a partial pressure of $2.0 \times 10^{-5}$ Torr Ar in the chamber. The ion
energy was 500 eV. Bombardment of the Si(100) surface occurred at 600 K at an ion current of 0.5 μA/cm² for approximately 180 minutes at several different orientations of the crystal with respect to the sputter gun to allow for uniform SiO₂ film deposition. The deposition was followed by cooling the crystal in O₂, leading to the production of a layer of SiO₂, which passivates the Si(100) surface. The SiO₂ layer thickness for the annealed film (900 K) was estimated from the attenuation of the 92 eV Si (LVV) Auger feature. This attenuation corresponds to a SiO₂ film thickness of 20 Å ± 5 Å if an electron attenuation length of 6.5 Å is employed [28]. This method provides a clean reproducible SiO₂ substrate for sequential experiments.

A collimated and calibrated multicapillary array doser (doser temperature = 300 K) was employed to reproducibly dose the substrate surface [21]. The multicapillary array doser contained a 2.2 cm diameter glass multicapillary collimator array composed of closely spaced 10 μm inside-diameter capillaries of 500 μm length. The flux from the doser was controlled by a fixed, nominally 5 μm diameter, orifice seated inside the doser by adjusting the backing pressure of TMG in the gas line. The doser conductance was measured using N₂, and on this basis the calculated effusion rate of TMG is $4.14 \times 10^{12}$ TMG molecules/Torr sec. Using the geometry of the doser and crystal [29], this effusion rate is equivalent to a flux at the SiO₂ substrate of $1.4 \times 10^{12}$ TMG molecules/cm² Torr sec. A shutter between the doser and crystal served to start and stop the adsorption step. Recent studies have shown that essentially pure TMG may be delivered in this manner [30].

Trimethylgallium was obtained from Strem Chemicals in a stainless steel cylinder. It was further purified by freeze-pump-thaw cycles inside the stainless steel gas handling line. Typical pressures of 2.0 Torr were used behind the conductance limiting orifice of the dosing system and measured to an accuracy of
± 0.001 Torr using a Baratron capacitance manometer.

III. Experimental Results

A. Adsorption of TMG on SiO₂/Si(100)

The adsorption of TMG on SiO₂ at 97 K to the extent of approximately one monolayer was monitored in several ways. The first method employed Auger electron spectroscopy (AES) measurements at different intervals during the adsorption. Each Auger measurement was done at a different position on the SiO₂ surface during the stepwise adsorption. AES measurements of the peak-to-peak intensity of the Si(LVV) 76 eV feature shown in Fig. 2 and the C(KLL) 272 eV feature in Fig. 3 both reveal a break point at 1.4 × 10^{14} TMG molecules/cm² delivered to the SiO₂ substrate. This break point is indicative of a cross over from monolayer to multilayer adsorption likely accompanied by a decrease in sticking probability occurring near the formation of monolayer coverage. This identification of the monolayer exposure can be qualitatively checked by comparison to an ideal situation by considering the TMG molecules (modeled as 7 Å diameter disks [31]) to adsorb in a close-packed manner. This yields an estimate of 2.4 × 10^{14} molecules/cm² of TMG for the saturated monolayer, in fair agreement with the breakpoint observed at an exposure of 1.4 × 10^{14} molecules/cm².

The AES measurement conditions introduce the effect of electron stimulated desorption (ESD) into the measurement of surface coverage. The Auger signals for carbon from a monolayer of TMG are shown in Fig. 4 and for gallium in Fig. 5 as a function of the extent of bombardment by the 3 kV electron beam. The ESD effect is significant for high electron doses, but relatively
insignificant for the electron doses used here.

All AES measurements following treatment of the gallium alkyl layer with atomic H were obtained by averaging over at least three points on the substrate and were made using a standardized electron dosage schedule and working within the region of electron dosage where the carbon or gallium desorption is negligible. However, both the carbon and gallium Auger signals are likely to be from surface species which have been decomposed by the electron beam. Hence these Auger intensities are indicators of the local carbon and gallium assay following electron beam induced decomposition of the adsorbed species.

The second method used to estimate TMG monolayer exposure and coverage is based on thermal desorption data. TMG has a mass spectrometer cracking pattern consisting mainly of CH$_4^+$ (m/e = 16), Ga$^+$ (m/e = 69), Ga(CH$_3$)$_2^+$ (m/e = 84; monomethylgallium, MMG), Ga(CH$_3$)$_2^+$ (m/e = 99; dimethylgallium, DMG), and Ga(CH$_3$)$_3^+$, (m/e = 114). The TPD yield versus TMG fluence in Fig. 6 shows that no TMG (m/e = 114, TMG) starts to desorb until reaching TMG exposures corresponding approximately to the formation of the second layer based on the calibrated doser results and AES measurements.

These observations (Fig. 6) indicate that the adsorption of TMG as a monolayer on SiO$_2$ produces primarily DMG as a thermal desorption product. The data may indicate that DMG is produced during adsorption of TMG on the SiO$_2$ in the first monolayer. Morrow and McFarlane [32] in fact have found that Si-O-Si groups in the surface of SiO$_2$ react with TMG to produce DMG surface species. This first layer is designated Ga(CH$_3$)$_x$. Above the monolayer coverage, TMG remains stable during heating and desorption. Detailed information about the thermal desorption from layers produced by TMG adsorption is provided later in this paper.
B. Extraction of CH₃ Groups by Atomic Hydrogen

Exposure of atomic hydrogen to the Ga(CH₃)ₓ monolayer on the SiO₂ surface was carried out at three different substrate temperatures (97 K, 108 K and 138 K) resulting in quantitative removal of methyl groups. The results are presented on the left-hand side of Fig. 7. The experimental points shown in all three experiments were measured following controlled exposure at constant atomic hydrogen flux, so that the relative rates of methyl removal can be accurately compared. Since each of the Auger measurements were made at points not affected by the electron beam previously, the depletion of carbon is due almost entirely to atomic H exposure. The dosage of atomic hydrogen is measured in terms of monolayers of H atoms incident as defined in the Experimental section. The data show that the C(KLL) Auger signal decreases to zero while the Ga(LMM) Auger signal undergoes relatively small changes as atomic hydrogen is incident on the adsorbed Ga(CH₃)ₓ species. A slight decrease in the Ga(LMM) Auger intensity is observed at the start, followed by a gradual increase until all carbon is seen to be removed, and the Ga(LMM) Auger intensity then remains constant. The reason for the characteristic initial slight decrease in the Ga Auger signal during CH₃ removal is currently unknown. The increase over most of the range of the experiment is undoubtedly due to the reduction in screening of the Ga by CH₃ groups as CH₃ groups are removed by the atomic H.

The data on the right-hand side of Fig. 7 are replotted as semilogarithmic plots in accordance with first-order kinetic behavior. The linear regression analysis gives a straight line with a slope, m, that is proportional to the first-order rate constant for CH₃ removal. As seen, the slopes and hence the rate constant for
the atomic-H induced methyl extraction, over a temperature range of 41 K, is constant within the experimental errors in the rate measurement. This gives an activation energy of zero for the CH$_3$ extraction process. The errors in this measurement correspond to an activation energy of $0^{+0.09}_{-0.02}$ kcal/mole for the CH$_3$ extraction by atomic H.

C. Thermal Desorption Studies Following Atomic Hydrogen Exposure

Typical thermal desorption data are shown for the 108 K-atomic H extraction experiments in Figs. 8-9 for a starting coverage derived from one monolayer of TMG exposed to varying dosages of atomic hydrogen. In Fig. 8 it is apparent that the DMG monolayer (produced from TMG adsorption on SiO$_2$) is systematically depleted by atomic hydrogen dosing at 108 K, until all DMG is destroyed. Following ~ 200 monolayers of atomic H exposure, no DMG cracking product is visible upon subsequent thermal desorption. Auger spectroscopy reveals that Ga is still present as seen in Fig. 7. Supporting evidence is obtained from additional studies of the Ga$^+$ (m/e = 69) cracking product produced in TPD following atomic hydrogen dosing as shown in Fig. 9. Here too, depletion of Ga(CH$_3$)$_2$ by atomic H exposure is indicated.

The depletion of the Ga$^+$ (m/e = 69) cracking product due to decomposition of Ga(CH$_3$)$_2$ by atomic hydrogen (Fig. 9) is accompanied by the deposition of metallic Ga which is strongly bound to the SiO$_2$ substrate, and which desorbs at much higher temperature. Auger studies of the thermal behavior of metallic Ga produced in this manner were performed as shown in Fig. 10, indicating that the Ga layer is fairly stable over the temperature range from 100 K - 700 K. Near 900 K, the SiO$_2$ layer on Si becomes unstable as SiO(g) desorbs and this process may
be related to the final thermal depletion of Ga.

IV. Discussion

A. Postulated Mechanism for H Atom Extraction of CH₃ Groups

As this experimental work was being carried out, a theoretical analysis of the interaction of atomic hydrogen with the trimethylaluminum molecule was published by Hiraoka and Mashita [33]. The *ab initio* molecular orbital calculations indicated that the two elementary steps shown below were of low activation energy, much less than the dissociation energy of the Al-CH₃ bond.

\[
\text{AlH}_2\text{CH}_3 + \text{H} \rightarrow \text{AlH}_3 + \text{CH}_3, \quad E_a = 1.9 \text{ kcal/mole} \quad (1)
\]

\[
\text{AlH}_2\text{CH}_3 + \text{H} \rightarrow \text{AlH}_2 + \text{CH}_4, \quad E_a = 12.7 \text{ kcal/mole} \quad (2)
\]

In the Hiraoka-Mashita calculation, the AlH₂CH₃ molecule was taken to represent the Al(CH₃)₃ molecule. The Al-CH₃ bond in AlH₂CH₃ has a dissociation energy of 77.1 kcal/mole[33], to form AlH₂ + CH₃.

The transition state for reaction (2) was determined to be a linear H₂Al···H···CH₃ complex which is a classical H atom insertion type complex. However, a lower energy local minimum was also observed for the species of C₃ᵥ symmetry having the structure H₂Al-CH₃, and this minimum energy structure was postulated to form in the early stage of the progress of the reaction along the
reaction coordinate leading to either reaction (1) or reaction (2).

The chemistry of Ga(CH₃)₃ has been explored recently under hydrogenation conditions by others[34], finding direct evidence for the production of (CH₃)₂Ga(μ-H)₂Ga(CH₃)₂ molecules which are stable at 290 K. This investigation forms the first definitive structural characterization of a compound containing two Ga atoms linked by a hydrogen bridge. In addition, evidence for trimeric or higher polymers of the form [(CH₃)₂GaH]ₙ was also obtained[34].

The ab initio calculations[33] and the structural determination of the replacement of a Ga-CH₃ bond by a bridging H bond[34] leave little doubt that similar chemistry may be achieved by the exposure of surface species containing Ga-CH₃ bonds to atomic H, as demonstrated in the research reported here.

The ab initio calculation[33] and the direct observation of hydrogen bridging between Ga atoms which have lost a CH₃ group [34] both indicate that H atom attack of the Ga atom occurs first, followed by elimination of CH₃ with the formation of either a CH₃ radical or CH₄. Our studies do not discriminate between CH₃ and CH₄ formation for Ga(CH₃)ₓ species, although the zero activation energy measured may suggest that CH₃ elimination is favored in Ga(CH₃)ₓ by analogy to the result calculated theoretically for reaction (1).

B. Relationship to MOCVD Production of III-V Compounds

This new reaction, involving H atom insertion into Ga-CH₃ bonds, could be very important in MOCVD processes in which atomic H is present. The elimination of CH₃ groups from metal alkyl molecules by atomic hydrogen can occur both in the gas phase as well as on the surface of the growing film. The use of atomic H provides a facile route for the elimination of carbon from the III-V
film growth process, either by displacement of CH$_3$ groups and/or by the formation of CH$_4$. As will be shown in a subsequent paper, we have used the H atom insertion process to eliminate CH$_3$ groups during the growth of a GaN film, where the electron bombardment of NH$_3$ has served to provide a local source of H atoms[19].

V. Summary

Atomic H has been used to eliminate CH$_3$ groups from a monolayer film derived from Ga(CH$_3$)$_3$ and supported on a SiO$_2$ film. The following observations about this reaction have been made:

1. The reaction between Ga(CH$_3$)$_x$ and atomic H occurs near 100 K with the elimination of carbon either as CH$_3$ and/or CH$_4$.

2. The efficiency of the reaction per incident H atom is of order 10$^{-2}$. Approximately 100 monolayers of incident H result in better than 95% elimination of C, as determined using both Auger spectroscopy and thermal desorption methods.

3. The activation energy for the CH$_3$ extraction reaction by atomic H is zero. Based on this observation the reaction may be of the Eley-Rideal type, although other studies are needed to definitely establish the mechanism.

4. The reaction is first-order in CH$_3$ coverage on the surface.
5. The observation of this reaction confirms theoretical expectations based on \textit{ab initio} studies of the related AlH$_2$(CH$_3$) molecule, where efficient H atom insertion in the Al-C bond was found to occur via low activation energy processes.

6. This work demonstrates how mechanistic information about high temperature surface processes may often be obtained by working at low temperatures where appreciable surface coverages of reactant molecules may be maintained on the surface for kinetic investigation.

Acknowledgement

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References

   3(b) H.P. Maruska and J.J. Tietjen, Appl. Phys. Lett, 15, 327 (1969); see also ref. 1.


Figure Captions

Figure 1. Development of hydrogen coverage on Si(100) at 600 K. The monohydride saturation coverage corresponds to $6.8 \times 10^{14}$ H/cm$^2$ on the perfect Si(100) surface.

Figure 2. Auger spectroscopy study of the adsorption of trimethylgallium on SiO$_2$/Si(100) at 97 K. The attenuation of the Si(LVV) Auger intensity is followed, sampling a new position on the surface for each point. The monolayer coverage is shown at the dotted line.

Figure 3. Auger spectroscopy study of the adsorption of trimethylgallium on SiO$_2$/Si(100) at 97 K. The growth of the C(KLL) Auger intensity is followed, sampling a new position on the surface for each point. The monolayer coverage is shown at the dotted line.

Figure 4. Effect of prolonged electron beam exposure on the carbon Auger intensity measured for one monolayer of trimethylgallium on SiO$_2$/Si(100). The electron beam remains on one spot during continuous irradiation. The data show that the effect of the electron beam on the C(KLL) intensity is small during the time required to make one measurement.
Figure 5. Effect of prolonged electron beam exposure on the gallium Auger intensity measured for one monolayer of trimethylgallium on SiO$_2$/Si(100). The electron beam remains on one spot during continuous irradiation. The data show that the effect of the electron beam on the Ga(LMM) intensity is small during the time required to make one measurement.

Figure 6. Time integrated yields of mass spectrometer fragments from trimethylgallium-derived layers on SiO$_2$/Si(100). The adsorption temperature was 97 K. Above the one monolayer coverage, the desorption of TMG begins to be observed at m/e = 114. For coverages in the first monolayer, the mass spectrometer detects only DMG at m/e = 99. This suggests that the first layer may be DMG at 97 K adsorption temperature.

Figure 7. Kinetics of extraction by atomic H of CH$_3$ from one monolayer of Ga(CH$_3$)$_x$ on SiO$_2$/Si(100) at three temperatures. The behavior of both the C(KLL) and the Ga(LMM) Auger intensities are shown on the left. Auger intensities are measured at different spots on the surface for each point. On the right, a semilog plot of the behavior of the C(KLL) signal is shown. Within experimental error, the slope of the first order plot, m, is constant over a 41 K temperature range, indicating that atomic H extraction of CH$_3$ groups is non-activated.

Figure 8. Depletion of the m/e = 99 thermal desorption feature following various atomic H exposures at 108 K. Complete loss of this product is observed for approximately 100 ML of atomic H exposure.
Figure 9. Depletion of the m/e = 69 thermal desorption feature following various atomic H exposures at 108 K. Complete loss of this product is observed for approximately 100 ML of atomic H exposure. Subsequent Auger studies show that Ga remains on the surface following this treatment.

Figure 10. Thermal stability of the gallium film produced by complete removal of CH3 groups using atomic H. Auger spectroscopy is employed for these measurements.
DEVELOPMENT OF HYDROGEN COVERAGE
ON Si(100)

$\rho_{H_2} = 2.0 \times 10^{-7}$ Torr
XTAL TEMP. = 600 K

MONOHYDRIDE SATURATION
ADSORPTION OF TRIMETHYLGALLIUM ON SiO$_2$/Si(100)

![Graph showing the relationship between TMG fluence and carbon KLL Auger intensity.](image)

- **Carbon(KLL) Auger intensity (arb. units)**
- **TMG Fluence ($\times 10^{14}$/cm$^2$)**

**1 MONOLAYER**

$T_{ads} = 97$ K
ADSORPTION OF TRIMETHYLGALLIUM ON SiO$_2$/Si(100)

\[ T_{ads} = 97 \text{ K} \]

Silicon(LV) Auger intensity (arb. units) vs. TMG fluence ($\times 10^{14}$/cm$^2$)
EFFECT OF PROLONGED ELECTRON BEAM EXPOSURE ON TMG/SiO₂

I = 3.0 μA
V = 3 kV
T = 97 K

CARBON AUGER INTENSITY (arb. units)

ELECTRON EXPOSURE REQUIRED FOR ONE AUGER MEASUREMENT

ELECTRON FLUENCE (×10¹⁸ e/cm²)
EFFECT OF PROLONGED ELECTRON BEAM EXPOSURE ON TMG/SiO₂

- I = 3.0 µA
- V = 3 kV
- T = 97 K

ELECTRON EXPOSURE REQUIRED FOR ONE AUGER MEASUREMENT

GALLIUM AUGER INTENSITY (arb. units)

ELECTRON FLUENCE (×10^{18} e/cm²)
THERMAL DESORPTION OF m/e=99 and m/e=114 FROM SiO₂ EXPOSED TO TMG

![Graph showing QMS SIGNAL vs. TMG FLUENCE](image)
KINETICS OF EXTRACTION OF CH₃ FROM Ga(CH₃)ₓ BY ATOMIC HYDROGEN AT DIFFERENT TEMPERATURES

Figure
THERMAL DESORPTION SERIES (m/e=99) FOR TMG ON SiO$_2$

$T=108$ K

DESORPTION SIGNAL (arb.units)

TEMPerATURE (K)

200 MONOLAYERS H
80 MONOLAYERS H
60 MONOLAYERS H
45 MONOLAYERS H
20 MONOLAYERS H
NO HYDROGEN

Lucas, et a

Figure 8
THERMAL DESORPTION SERIES (m/e=69) FOR TMG ON SiO$_2$  

T=108 K

200 MONOLAYERS H

80 MONOLAYERS H

60 MONOLAYERS H

45 MONOLAYERS H

20 MONOLAYERS H

NO HYDROGEN

DESORPTION SIGNAL (arb. units)

TEMPERATURE (K)

Lucas, et  

Figure 9
THERMAL STABILITY OF GALLIUM FILM PRODUCED ON SiO$_2$/Si(100) BY ATOMIC HYDROGEN EXPOSURE OF Ga(CH$_3$)$_x$/SiO$_2$/Si(100) AT 108 K
7. APPENDIX 2

GaN Patterned Film Synthesis - Carbon Depletion by Hydrogen Atoms
Produced from NH₃ Activated by Electron Impact

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GaN Patterned Film Synthesis - Carbon Depletion by Hydrogen Atoms
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Abstract

The electron induced reaction of NH₃ with a surface layer produced by adsorption of trimethylgallium (TMG) on SiO₂ at 108 K has been investigated by Auger electron spectroscopy. It is shown that atomic hydrogen, produced by electron induced dissociation of NH₃, to form NHₓ and H, efficiently extracts the methyl-groups from the layer leading to carbon removal from the GaN film which is formed. This process is non-thermal. A procedure for the synthesis of GaN is demonstrated and the layer-by-layer growth of a GaN film is shown. The method permits GaN to be deposited in a localized region which has been bombarded by the electron beam.
1. Introduction

GaN having a wide direct bandgap (3.4 eV at 300 K) is of great interest as an optoelectronic material applicable for blue and violet emitting devices working possibly at high temperatures [1,2]. Therefore the fabrication of high quality GaN films is required. Usually, GaN films are grown by metal organic molecular beam epitaxy (MOMBE) or metal organic chemical vapor deposition (MOCVD) methods. However, growth by these traditional techniques is accompanied by a variety of problems [2,3]. A possible major problem could be carbon contamination of the GaN films during the reaction of metal organics such as trimethylgallium (TMG) with NH₃, as seen for example in GaAs growth [4].

Previous studies have shown that atomic hydrogen extracts the methyl-groups from trimethylgallium-derived layers by producing either CH₃(g) or CH₄(g) [5]. This reaction is thought to be an Eley-Rideal process. The reaction occurs with an efficiency of 10⁻² near 100 K and is non-activated [5]. Building on these first observations of the active role of atomic hydrogen in extracting CH₃ groups from the Ga-CH₃ bond, we have developed a second method which removes CH₃ groups efficiently while simultaneously synthesizing a GaN film. The source for atomic hydrogen is NH₃. It has been found previously that electron bombardment induces the dissociation of chemisorbed NH₃ to chemisorbed NH₂ [6] and chemisorbed NH [7] on Ni(110) producing atomic hydrogen at the surface. In addition Singh et al. [8] reported the dissociation of NH₃ to NH₂ on GaAs(100) following irradiation by 10 eV electrons at 150 K. This method has also been used successfully for low temperature electron-impact-induced nitridation of GaAs(100) [9] and SiO₂ thin films [10] using NH₃.

This study concerns the effect of electron impact on TMG-derived layers in the presence of adsorbed NH₃. The results provide a new method for the
production of GaN films under reaction conditions where carbon is directly eliminated from the surface. This new technique is utilized to grow monolayer and multilayer films of GaN and to show that direct writing of GaN features with an electron beam is possible, using the new technique.

2. Experimental

The experiments were carried out in an ultra-high vacuum (UHV) chamber with a base pressure of $p = 1 \times 10^{-10}$ Torr. The system is equipped with a cylindrical mirror analyzer (CMA) Auger electron spectrometer (AES), an Ar$^+$-ion sputter gun, a multiplexed quadrupole mass spectrometer, a reverse view low energy electron diffraction (LEED) apparatus and a calibrated microcapillary array doser [11-13]. The mounting procedure for the Si(100) crystal (p-type, B doped, 10 $\Omega\cdot$cm, $13 \times 13 \times 1.5$ mm$^3$) has been described previously [11, 13]. Final crystal cleaning is achieved by sputtering with Ar$^+$-ions ($E_i = 2$ keV, $I_{Ar^+} = 3.0$ $\mu$A) and subsequent heating to 1200 K. The heating is carried out resistively using a temperature programmer. SiO$_2$ films were prepared on the clean Si(100) crystal in the UHV chamber by a sputter-oxidation technique which employed approximately equal Ar and O$_2$ backing pressures ($p_{Ar} = p_{O_2} = 2 \times 10^{-5}$ Torr) [5] following the procedure of Chen et al., described previously [14]. An ion energy of 500 eV was employed. The thickness of the as-formed SiO$_2$ film was estimated to be 15-25 Å using the attenuation of the Si$^0$ (92 eV) Auger feature characteristic of the underlying Si(100) substrate and assuming an electron escape depth of 6.5 Å for SiO$_2$ [15]. Trimethylgallium (99.9999 % pure, Strem Chemicals) (TMG) was further purified by a freeze - pump - thaw cycle. The gas molecules were delivered to the crystal surface through the beam doser. Other studies indicate that almost pure TMG is emitted from the doser under the conditions of this experiment [16].
The adsorption/desorption kinetics for TMG on SiO₂ have been studied previously using Auger spectroscopy and temperature programmed desorption (TPD) [5] making it possible to estimate the layer thickness deposited in terms of monolayers.

All electron and ion beam currents (I) reported here were those measured between the crystal and ground and are uncorrected for secondary electron yield. The AES measurements were carried out with a 3 keV primary excitation electron beam which delivered Iₑ = 3 µA of current to the surface. The diameter of the electron beam was measured to be ~ 0.3 mm by translating the edge of the crystal through the electron beam and measuring the collected current. The modulation voltage was set at 6 V peak-to-peak for AES intensity measurements and 2 V peak-to-peak for AES line shape observations, respectively. The electron beam exposure used in these measurements was shown not to produce significant carbon depletion in control experiments carried out without a source of atomic hydrogen being present.

3. Results and Discussion

A. Electron-induced reaction of NH₃ with Ga(CH₃)ₓ/SiO₂

It has been shown by thermal desorption measurements that an adsorbed monolayer produced from TMG on SiO₂ probably consists of Ga(CH₃)₂, based on observations of the thermal desorption of this species at ~ 155 K [5]. We designate this layer as Ga(CH₃)ₓ. The effect of NH₃ and electron impact on Ga(CH₃)ₓ/SiO₂ was measured by adsorbing approximately 1 monolayer of TMG on SiO₂/Si(100) at 108 K [5], backfilling the chamber with various pressures of NH₃ and exposing the crystal to a 3 keV electron beam for a pre-determined time. The electron
exposure was carried out in a duty cycle of 40 s active exposure time and 30 s with the crystal out of the electron beam to avoid large charging effects. Figure 1 shows the C (KLL) AES signal intensity (left side) and its natural logarithm (right side) versus the electron fluence for various NH$_3$ pressures.

While there is only a weak electron induced-desorption of carbon without NH$_3$ in the chamber, a strong decrease in the C (KLL) signal is observed when the NH$_3$ pressure is increased. Assuming first-order kinetics for the electron impact induced reaction, a cross section, $Q_{p_{NH3}}$, for this process may be evaluated from the expression:

$$N_c = N_c^0 \exp[-(j/e)Q_{p_{NH3}}].$$  \hspace{1cm} (1)

Here $N_c$ and $N_c^0$ are the coverage of carbon atoms at the time $t$ and at the time $t = 0$, respectively, $j$ is the electron irradiation current density and $e$ is the elementary charge. The cross section determined from this analysis, $Q_{p_{NH3}}$, is dependent on the pressure of NH$_3$ because of the dependence of the rate of the electron-induced process on the steady state coverage of NH$_3$ achieved under dynamic conditions.

In addition to measurements of carbon depletion due to electron induced-processes, it was important to monitor Ga depletion effects also. In the Ga (LMM) Auger measurements (Figure 2), almost no difference between the "no NH$_3"-curve (background pressure of $\sim 1 \times 10^{-10}$ Torr) and the curves at the various NH$_3$ pressures is seen. This clearly indicates that the major electron-induced process in the presence of NH$_3$ is the removal of the methyl-groups, while Ga remains on the surface. The Ga Auger intensity was shown to be stable up to $\sim 900$ K, as would be expected for GaN.

A control experiment with N$_2$ instead of NH$_3$ was employed to distinguish between the role of electron-induced formation of N and H in the reaction. Figure
3 shows clearly that even at a N$_2$ pressure of p$_{N_2}$ = 5 × 10$^{-8}$ Torr there is no influence (within the experimental uncertainty) on the rate of the C(KLL) and the Ga(LMM) loss processes. This leads to the conclusion that H derived from electron-induced dissociation of NH$_3$ (a) is needed for the extraction of the methyl-groups.

Previous studies on the effect of atomic hydrogen on TMG/SiO$_2$ [5] and the results presented here lead to the postulated mechanism shown schematically in Figure 4:

a) Electron-induced dissociation of adsorbed NH$_3$ [6,7,8] leads to the production of NH$_X$ (a) and H species. Since we employ a 3 keV electron beam it is very likely that backscattered and/or secondary electrons returning from the bulk to the surface play an important role in this process.

b) Atomic hydrogen reacts with the methyl-groups of Ga(CH$_3$)$_X$/SiO$_2$ eliminating CH$_3$ groups efficiently.

c) During the irradiation with electrons GaN is formed. The GaN is thermally stable to 900 K.

The mechanism accounts for increase of the cross section, $Q_{p_{NH_3}}$, with increasing ammonia pressure, since the surface coverage of adsorbed NH$_3$ under dynamic conditions, and hence the supply of atomic hydrogen, will increase with increasing p$_{NH_3}$. Atomic hydrogen made from NH$_3$ removes the methyl-groups from TMG. The rate of extraction of the methyl-groups increases with the rate of production of hydrogen atoms from NH$_3$ on the surface. As indicated by linear semilog plots in Fig. 1, the reaction is first-order in the surface concentration of CH$_3$ groups at a given p$_{NH_3}$. The cross section, $Q_{p_{NH_3}}$, for depletion of carbon is of the order of 5 × 10$^{-20}$ cm$^2$ at p$_{NH_3}$ = 5 × 10$^{-8}$ Torr.

It is of interest to compare the rate of the CH$_3$ depletion process with the flux of electrons and the flux of NH$_3$ onto the surface under these conditions. At
the beginning of the CH₃ extraction process, we assume that a monolayer of the Ga(CH₃)ₓ consists of about 1 × 10¹⁴ species/cm² = N [5]. Then, for an electron flux,

\[ F_e \approx 2 \times 10^{16} \text{ e} / (\text{cm}^2 \text{ s}), \]

\[ -\frac{dN}{dt} = N F_e \Omega_{PNH_3} \approx 1 \times 10^{11} / (\text{cm}^2 \text{ s}) \]  \hspace{1cm} (2)

= rate of CH₃ loss.

Under these conditions, the flux of NH₃, F₂NH₃, from kinetic theory is ~200 times larger than the rate of the CH₃ loss, viz.

\[ F_{NH_3} = p_{NH_3} / (2\pi m_{NH_3} k T_g)^{\frac{1}{2}} \approx 2 \times 10^{13} \text{ NH}_3 / (\text{cm}^2 \text{ s}) \]  \hspace{1cm} (3)

Thus, under the conditions of the experiment, as shown by the information in equation (2), each electron has an efficiency of order 5×10⁻⁶ for causing a CH₃ extraction process. Assuming that electron stimulated desorption (ESD) effects have not caused significant depletion of NH₃ from a monolayer under the conditions of this experiment, a CH₃ extraction efficiency of 5×10⁻⁶ is reasonable on the following grounds:

a) Two inefficient processes work in series causing the extraction process.

They are:

\[ NH_3 + e^- \xrightarrow{\epsilon_1} NH_2 + H \]  \hspace{1cm} (4)

\[ H + Ga(CH_3)_x \xrightarrow{\epsilon_2} HGa(CH_3)_{x-1} + CH_3(g) \text{ or } CH_4(g) \]  \hspace{1cm} (5)

where \( \epsilon_1 \) is the efficiency to produce one H per collision of one electron with NH₃ (a) and \( \epsilon_2 \) is the efficiency of CH₃ extraction by the atomic H produced as described by equation (4).

b) We know, from previous studies of the CH₃ extraction process by atomic H, that an efficiency of order 10⁻² is appropriate for \( \epsilon_2 \) [5].

c) Thus, since the joint efficiency \( \epsilon_2 \epsilon_1 \) is \( \sim 5 \times 10^{-6} \) / electron, \( \epsilon_1 \) is \( \sim 5 \times 10^{-4} \), corresponding to a cross section of order \( 5 \times 10^{-19} \) cm² for breaking
the N-H bond in adsorbed NH$_3$ by electron impact using 3 keV electrons (assuming a NH$_3$ coverage of the order of $10^{15}$/cm$^2$).

A value of $\sim 10^{-16}$ cm$^2$ for N-H bond breaking in chemisorbed NH$_3$ by 55 eV electrons has been measured on a Ni(110) surface [6].

B. GaN growth

Applying the above method, it is possible to grow GaN on SiO$_2$ as schematically shown in Fig. 4. GaN is produced from this treatment and the Ga(LMM) and the N(KLL) Auger intensities were observed to be stable to 900 K in the electron irradiated spot, while elsewhere (without electron exposure) the N(KLL) and the Ga(LMM) AES intensities fell to near zero at 900 K, as thermal desorption of non-reacted species occurred.

Figure 5 shows the N(KLL) Auger signal from Si$_3$N$_4$ [17], and also of a monolayer and a multilayer of the as-formed GaN on SiO$_2$. In addition the measured N(KLL) lineshape of a 1.23 $\mu$m thick GaN film on (0001)Al$_2$O$_3$ (grown by metal-organic chemical vapor deposition) was used as a reference. With increasing thickness of the GaN film grown by the process described in this paper, the N(KLL) lineshape becomes increasingly similar to that of the GaN reference; however, the characteristic nitride Auger lineshape was not observed.

In Fig. 5, a superposition of the GaN and a Si$_3$N$_4$ N(KLL) Auger signal is present. After adsorption of approximately 1 monolayer of TMG on SiO$_2$ and methyl-group extraction by NH$_3$ activated by electron impact, both GaN and Si$_3$N$_4$ will be detected by AES. With increasing thickness of the GaN film, the N(KLL) Auger lineshape will approach that of GaN, but as long as the thickness of the GaN film is in the order of the escape depth for Auger electrons ($\sim 10$ Å for 380 eV electrons [18]) there will be a contribution from Si$_3$N$_4$ also, as seen in Figure
5. This may contribute to the lack of exact agreement in the N(KLL) Auger lineshape with the GaN standard.

The GaN film growth in three steps is shown in Figure 6 together with the corresponding C(KLL), N(KLL) and Ga(LMM) AES signals. In step one, approximately 1 monolayer of TMG is adsorbed on the SiO$_2$/Si(100) surface at 108 K [5] so that in addition to the Si and the O Auger signals, also the C and the Ga signals due to the TMG-derived layer are visible. In the second step the chamber is backfilled with $p_{\text{NH}_3}=5\times10^{-7}$ Torr of ammonia and the crystal is exposed to the 3 keV Auger electron beam (I = 3μA) for 15 min. The C(KLL) signal disappears due to the reaction of H atoms (produced from adsorbed NH$_3$) with the surface methyl-groups and the N(KLL) signal develops indicating that GaN and adsorbed NH$_X$ are present; the Ga Auger intensity remains the same as in step one. In step three, subsequent heating to 300 K yields an Auger spectrum which indicates no carbon; only N and Ga are present. Auger spectra acquired on areas of the SiO$_2$ surface not subjected to electron irradiation in the presence of NH$_3$ (g) show that 300 K is sufficient to desorb NH$_3$ and the Ga(CH$_3$)$_X$, as shown at the bottom of Figure 6.

Repeated use of this procedure leads to a multilayer of GaN (Figure 7). After the growth of the first layer the crystal was heated to 300 K (2nd row) and after the growth of the second layer the crystal was heated up to 900 K (4th row). AES measurements outside the actual GaN dot (5th row) show almost no C, Ga or N, indicating that the GaN synthesis reaction takes place only where the crystal containing Ga(CH$_3$)$_X$ and NH$_3$ layers is exposed to electrons.

The procedure to produce a dot of GaN was modified to produce a line of GaN and an AES profile perpendicular to the line was then acquired (Figure 8). This line was grown at 108 K without heating subsequently, so that outside the line both Ga(CH$_3$)$_X$ and NH$_3$ remain adsorbed. The C(KLL) signal is low on the
GaN line due to the electron-induced reaction of atomic H from NH₃ with the surface methyl-groups. Off the line the C(KLL) signal is high, indicating the presence of adsorbed Ga(CH₃)ₓ on both sides of the line. The N(KLL) signal shows opposite behavior. Outside the line adsorbed NH₃(low signal) is seen. In contrast, in the GaN line region the N(KLL) signal is quadrupled. The Ga(LMM) signal (not shown) exhibits a slight increase on the line as compared with its values acquired off the line. The data are arbitrarily fit to a Gaussian profile but the actual GaN lineshape cannot be determined in this experiment.

C. Extension to GaN Film Growth at Higher Substrate Temperatures

The SiO₂ substrate temperatures chosen for these studies was 108 K. This is done so that significant coverages of TMG and NH₃ can be maintained in ultrahigh vacuum, needed for the analytical procedure employed here. It is envisioned that growth of GaN by this method will work at higher substrate temperatures, using higher TMG and NH₃ pressures to maintain the appropriate surface coverage for efficient electron-impact induced GaN film growth.

4. Conclusions

Trimethylgallium and ammonia have been used as precursors for GaN formation, activated by electron impact. It is found that the methyl-groups are removed from TMG by a reaction with atomic hydrogen, formed by the electron-impact-induced dissociation of NH₃. This is consistent with earlier studies [5] in which atomic hydrogen, produced in the gas phase also efficiently removes methyl-groups. The mechanism has been applied to grow GaN on SiO₂ and it is shown that GaN-structure writing on SiO₂ is possible using the electron beam.
This synthesis method offers the possibility of producing GaN films which are less contaminated by carbon impurities than GaN films grown thermally from the same precursors.

Acknowledgment

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Figure captions

Figure 1. Electron induced reaction of NH$_3$ with Ga(CH$_3$)$_x$ / SiO$_2$. Shown is the C(KLL) Auger signal (left side) and its normalized natural logarithm (right side) versus the number of electrons per cm$^2$. $Q_{p_{NH_3}}$ is the NH$_3$ pressure dependent cross section for the depletion of the methyl-groups by the electron stimulated process.

Figure 2. Electron induced reaction of NH$_3$ with Ga(CH$_3$)$_x$ / SiO$_2$. Shown is the Ga(LMM) Auger signal (left side) and its normalized natural logarithm (right side) versus the number of electrons per cm$^2$.

Figure 3. Control experiment with N$_2$ instead of NH$_3$. Shown is the C(KLL) Auger signal and its normalized natural logarithm (top) and the Ga(LMM) Auger signal and its normalized natural logarithm (bottom) versus the number of electrons per cm$^2$.

Figure 4. Schematic mechanism for GaN production by an electron induced reaction of adsorbed Ga(CH$_3$)$_x$ with NH$_3$.

Figure 5. Normalized and superimposed lineshapes of the N(KLL) Auger signal with increasing thickness of the GaN film. A comparison to a reference thick film of GaN and a reference Si$_3$N$_4$ film is given. Modulation voltage = 2 V peak-to-peak.

Figure 6. Monolayer GaN synthesis on SiO$_2$ by an electron-induced reaction of Ga(CH$_3$)$_x$ with NH$_3$ at 108 K.

Figure 7. Multilayer GaN synthesis on SiO$_2$ by an electron-induced reaction of Ga(CH$_3$)$_x$ with NH$_3$ at 108 K.

Figure 8. Profile of C(KLL) and N(KLL) Auger signals across a GaN line grown according to the procedure of this paper by scanning the electron beam.
References


[17] The Si$_3$N$_4$ was prepared by an electron-induced nitridation of SiO$_2$, using NH$_3$ (see ref. 9).

Electron Induced Reaction of NH$_3$ with Ga(CH$_3$)$_x$/SiO$_2$

$I_{\text{crystal}} = 3\mu\text{A}$

$V_e = 3\text{kV}$

**Figure 1**

- **T = 108 K**
  - No NH$_3$ ($p_{\text{NH}_3} = 5 \cdot 10^{-9} \text{ Torr}$)
  - $Q_{p_{\text{NH}_3}} = (0.5 \pm 0.2) \cdot 10^{-20} \text{ cm}^2$

- No NH$_3$ (slope = $-0.3 \cdot 10^{-20}$)
  - $p_{\text{NH}_3} = 5 \cdot 10^{-8} \text{ Torr}$

- No NH$_3$ (slope = $-0.2 \cdot 10^{-20}$)
  - $p_{\text{NH}_3} = 1 \cdot 10^{-8} \text{ Torr}$

- No NH$_3$ (slope = $-0.3 \cdot 10^{-20}$)
  - $p_{\text{NH}_3} = 5 \cdot 10^{-8} \text{ Torr}$

- No NH$_3$ (slope = $-0.3 \cdot 10^{-20}$)
  - $p_{\text{NH}_3} = 5 \cdot 10^{-8} \text{ Torr}$

$Q_{p_{\text{NH}_3}} = (4.6 \pm 0.2) \cdot 10^{-20} \text{ cm}^2$
Electron Induced Reaction
of NH₃ with Ga(CH₃)ₓ/SiO₂

\[ I_{\text{crystal}} = 3 \mu A \]
\[ V_e = 3 \text{kV} \]

\[ T = 108 \text{ K} \]

\[ \ln \left( \frac{I}{I_0} \right) \left( \text{Ga(LMM)} \right) \]

\[ \text{No NH}_3 \]
\[ p_{\text{NH}_3} = 5 \cdot 10^{-9} \text{ Torr} \]

\[ \text{No NH}_3 \]
\[ p_{\text{NH}_3} = 1 \cdot 10^{-8} \text{ Torr} \]

\[ \text{No NH}_3 \]
\[ p_{\text{NH}_3} = 5 \cdot 10^{-8} \text{ Torr} \]

\[ N_e/\text{cm}^2 \left( \times 10^{19} \right) \]

\[ \text{Figure 2} \]

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Control Experiment - Electron Induced Reaction of N₂ with Ga(CH₃)ₓ/SiO₂

\[ I_{\text{crystal}} = 3 \mu A \]
\[ V_e = 3 \text{ kV} \]
Schematic Sequence of Reaction Events in Carbon Extraction and GaN Formation

SiO₂  
Si (100)  

T=108 K

Ga(CH₃)ₓ Ga(CH₃)ₓ Ga(CH₃)ₓ

NH₃  NHₓ  H⁺  NH₃

e⁻

Ga(CH₃)ₓ Ga(CH₃)ₓ Ga(CH₃)ₓ

SiO₂  
Si (100)  

T=108 K

Ga(CH₃)ₓ

CH₄

NH₃  NHₓ  H⁺  NH₃

e⁻

Ga(CH₃)ₓ

+ NH₃

SiO₂  
Si (100)  

T=108 K

Ga(CH₃)ₓ

GaN

SiO₂  
Si (100)  

T=900 K
Auger-Lineshapes of Si$_3$N$_4$ and GaN

![Graph showing Auger lineshapes for Si$_3$N$_4$ and GaN](image)

- **Si$_3$N$_4$ (reference)**
- **Mono GaN**
- **Multi GaN**
- **Bulk GaN (reference)**

**Electron Energy (eV)**

- dN(E)/dE
Monolayer GaN Synthesis on SiO₂
by using NH₃ + Electron Impact

Auger Spectrum

C
N
Ga

108 K

108 K

on GaN

300 K

on SiO₂

Electron Energy (eV)

200 250 300 350 400 1000 1100 1200
Multilayer GaN Synthesis

108 K

108 K, then warming up to 300 K

108 K

900 K

Auger Spectrum

C
N
Ga

Electron Energy (eV)

200 300 400 1000 1100
Profile of C and N over GaN-Line

![Graph showing the profile of C and N over GaN-Line with distance in mm on the x-axis and intensity on the y-axis. The graph includes markers for C(KLL) and N(KLL) with peaks and valleys indicating concentration variations.]
8. APPENDIX 3

Cathodoluminescence and FTIR Reflectance of Thin AlN and GaN Films

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ABSTRACT: Cathodoluminescence has been measured at several temperatures (300, 77, and 6 K) for thin (0.1 to = 5.0 \(\mu\)m) AlN and GaN films deposited on 6H SiC and sapphire substrates. Below band gap spectral features due to silicon in GaN and oxygen in AlN have been observed along with many other unexplained features. Room temperature infrared reflectance near the reststrahlen region has also been measured for these samples, providing information about the vibrational modes of the film material. These two optical techniques provide complementary characterization information for thin films.

Wide band gap nitride semiconductors are receiving a great deal of attention recently due to their possible applications for blue or ultraviolet solid state optical devices (Davis 1991). Two wide band gap nitrides currently under study are AlN and GaN, with band gaps of 6.2 eV (Maruska and Tietjen 1969) and 3.39 eV (Monemar 1974) respectively. Rapid characterization techniques are essential for the growth of high quality thin films. This paper presents data on thin AlN and GaN films deposited on 6H SiC and sapphire substrates using two characterization techniques, Fourier transform infrared (FTIR) reflectance and cathodoluminescence (CL), which provide complementary information.

The reflectance data from 400 - 5200 \(\text{cm}^{-1}\) are collected on a FTIR spectrometer using a KBr beamsplitter and a deuterated triglycine sulfate (DTGS) room temperature detector. The resolution of the spectra is 1 \(\text{cm}^{-1}\). The data are collected at near normal incidence (5°), using a 2000 \(\AA\) thick platinum film deposited on a sapphire substrate as the reflectance standard (Mantese et al. 1986). The spectra are not corrected for the reflectance of the Pt film.

The reflectance data are compared to calculated reflectance spectra based on Lorentz oscillator models for the frequency dependent infrared dielectric functions of the film and substrate materials. For GaN we use the results of Barker and Illegems (1973). For 6H SiC we use the model of Spitzer et al. (1959) with \(\varepsilon_0\) as given by Patrick and Choyke (1970). For sapphire we
use the multi-oscillator model of Barker (1963). Details of the reflectance calculation are given by MacMillan et al. (1993).

The CL spectra were collected at 6 K, 77 K, and 300 K on an instrument described in detail elsewhere (Partlow et al. 1990). The samples are mounted on a cold finger in a UHV chamber (5x10^{-11} torr). The luminescence is excited by an electron beam with energy in the range 5 to 10 keV. The luminescence is passed through a 1 meter Ebert monochromator to a liquid nitrogen cooled photomultiplier connected to either a photon counter or a lock-in amplifier.

Figure 1 shows the room temperature reflectance spectrum in the reststrahlen region of a 0.96 µm thick GaN film deposited on a 6H SiC substrate. Similar reflectance spectra have been seen in thin AlN films deposited on 6H SiC substrates which were analysed in detail by Mac Millan et al. (1993) and will not be discussed in this paper. The complicated structure seen in the GaN film samples is a result of both the film and the substrate having reststrahlen bands in the same region. The triangular shape of the GaN reststrahlen peak is due to the thinness of the film. The sharp dip in the spectrum at 733 cm^{-1} indicates the LO (A_1) vibrational frequency of GaN. This value does not agree with the value of 744 cm^{-1} obtained by Barker and Illegems (1973). However, their values for the vibrational frequencies were obtained from thin GaN films deposited on (0001) sapphire, which has a significant lattice mismatch with GaN. The lattice constant of 6H SiC is much closer to that of GaN and so any strain effects would be less (Strite and Morkoç 1992). Fabry-Perot fringes seen at higher frequencies (not shown on the figure) were used to determine the GaN film thickness.

Figure 2 shows the room temperature

FIG. 1. Relative reflectance of a 0.96 µm thick GaN film on a (0001)-6H SiC substrate. The solid line represents the data and the dashed line the calculated spectrum.

FIG. 2. Reflectance of a 4.52 µm thick GaN film on a sapphire substrate. The solid line represents the data and the dashed line the calculated spectrum.
reflectance spectrum in the reststrahlen region of a 4.52µm thick GaN film deposited on a sapphire substrate. Sapphire has several reststrahlen bands in this region, leading to the many reflectance peaks seen in the spectrum. For this film, the LO(A1) frequency is 743 cm⁻¹, which matches quite well with the Barker and Illegems (1973) value.

Figure 3 shows the low temperature (77 K) cathodoluminescence spectrum of a 4.48µm thick GaN film deposited on a sapphire substrate with a GaN buffer layer between the film and substrate. At this temperature the band gap of GaN is 3.5 eV (Monemar 1974). The small bump lying on the high energy side of the main emission peak at 3548Å has been attributed to free excitons (Dai et al. 1982). The main emission peak at 3567 Å is probably due to bound excitons (Dingle et al. 1971) The two side bands at 3646Å and 3751Å may be LO phonon replicas of the free exciton. This assignment was determined by using the LO phonon energy of 91.3 meV (737 cm⁻¹) obtained from the infrared reflectance spectrum of this sample.

Figure 4 shows the low temperature (77 K) cathodoluminescence spectrum of a 0.5 µm thick GaN film deposited on a 6H SiC substrate. This film was intentionally doped with Si to a level of 1.2 x 10¹⁸ cm⁻³. Silicon acts as an acceptor in GaN with an estimated binding energy of 225 meV (Khan et al. 1986). The peak located at 3775 Å (216 meV) is due to the presence of Si in the sample, but the mechanism for the luminescence has not yet been established.
Figure 5 shows both low temperature (6 K) and room temperature cathodoluminescence spectra of a 0.58μm thick AlN film deposited on a sapphire substrate in a UHV chamber. The peak centered at 3260Å is broad and does not shift with temperature. A similar peak was seen in polycrystalline AlN ceramics as well as one high purity single crystal AlN sample by Youngman et al. (1990), who attributed the feature to oxygen in the AlN.

Cathodoluminescence and room temperature reflectance spectra of thin GaN films deposited on SiC and sapphire substrates have been measured. Luminescence due to silicon impurities in GaN have been observed. Room temperature reflectance measurements on GaN films show that vibrational frequencies can be shifted for films deposited on different substrates. For GaN deposited on 6H SiC, LO(A1) = 733 cm⁻¹. For GaN deposited on sapphire with a buffer layer of either AlN or GaN, LO(A1) = 737 cm⁻¹. These values are quite different from the value LO(A1) = 744 cm⁻¹ obtained from GaN films deposited directly on sapphire. The cause of this shift is probably strain effects in the film, but this has not been proven. Information about the vibrational frequencies of the film material obtained from the reflectance spectra can be used to understand some of the features seen in the cathodoluminescence spectra.

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References