Hydrazine cyanurate as a nitrogen source for thin nitride film growth

Thomas J. Kropewnicki and Paul A. Kohl
School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

(Received 5 June 1997; accepted 5 September 1997)

The use of liquid hydrazine (N₂H₄) as a nitrogen source for nitridation reactions has been restricted because of safety, purity, and difficulties in using a liquid source. Hydrazine cyanurate (HC) is a stable solid complex of N₂H₄ which can be easily handled and purified before use and which evolves pure N₂H₄ upon heating, thus making it a promising source of N₂H₄ for nitridation reactions. In this article, a process for the synthesis of HC has been developed which decreases the H₂O content of the evolved N₂H₄ from 10% when H₂O was used as the solvent in the synthesis of HC to 0.7% by replacing H₂O with dimethylsulfoxide as the solvent in the synthesis of HC. The use of the purified HC is demonstrated as a solid source in the nitridation of (100) GaAs substrates at 200 °C in a low pressure chemical vapor deposition reactor. The nitridated GaAs surfaces were analyzed by x-ray photoelectron spectroscopy and were found to be primarily comprised of GaN, GaAs, and Ga₂O₃. The ratio of the constituent peak heights in the Ga 3d peak of GaN to Ga₂O₃ was 2.25 in the grown nitride films. The oxide impurities were most likely due to incomplete removal of the native substrate oxide formed prior to growth and were not a product of the nitridation. © 1998 American Vacuum Society. [S0734-2101(98)01301-3]

I. INTRODUCTION

Thin nitride films are important in many areas of microelectronics. For example, amorphous Si₃N₄ is a useful dielectric material in Si integrated circuits because it has a higher dielectric constant (ε = 5.5-9.4) than SiO₂ (ε = 3.8).¹ Si₃N₄ is also denser (ρ = 3.4 g/cm³) than SiO₂ (ρ = 2.2-2.6 g/cm³)² and thus is a better diffusion barrier to impurities. Thin films of TiN and WN have been used as contact metallization on Si to mitigate the problems of metal spiking and the formation of undesirable metal silicides. These metal nitride films have excellent thermal stability³ and low contact resistance to highly doped Si.⁴ Unlike Si, which has a passivating native oxide, the oxides of III–V semiconductors are of poor quality and often result in a high density of midgap trap states. These midgap traps cause high recombination velocities and leakage currents, which adversely affect the performance of devices such as field effect transistors and heterojunction bipolar transistors.⁵ Passivation of III–V semiconductor surfaces by nitridation has decreased the number of surface states in these materials and has improved the performance of III–V semiconductor devices.⁶

Wide band gap semiconductors with direct transitions are of interest because of their use in blue light emitting diodes and high temperature electronic devices.⁷ The Group III nitride semiconductors, which include AlN (Eg = 6.2 eV), GaN (Eg = 3.4 eV), InN (Eg = 1.9 eV), and their alloys are currently the focus of much research. Unfortunately, a suitable substrate for the growth of Group III nitride materials has not yet been found; the lattice mismatches between the nitrides and the available substrates can be as large as 15%.⁸ One way to initiate the growth of a nitride film is to convert the surface of a substrate to a nitride which may absorb some of the strain caused by the lattice mismatch at the interface between the substrate and the Group III nitride film to be grown. A method of nitridating the substrate surface without damaging it may be desirable for the epitaxial growth of Group III nitrides.

The nitridation of surfaces using N₂ is problematic because of its stability and bond strength (ΔH° = 946 kJ/mol).⁹ Surface nitrogen atoms can easily desorb as N₂, rather than reacting to form the desired nitride film. By increasing the surface mobility of the atomic nitrogen, the probability increases for the nitrogen atoms to form nitride bonds rather than desorbing as N₂. The high activation energy for N₂ requires high temperatures or plasma activation; however, high energy particles created in rf and electron cyclotron resonance plasmas can damage semiconductor surfaces,¹¹ final device performance may suffer.¹² Thus, alternate sources of active nitrogen species may be a critical enabling technology for nitride growth.

An alternative to activating N₂ by extreme physical conditions is to use a chemically energetic source of nitrogen. Three more reactive chemical sources of nitrogen have been used to grow nitride films; (i) ammonia (NH₃),¹³ (ii) hydrazine (N₂H₄),¹⁴ and its organic derivatives [e.g., monomethylhydrazine (NH₂NHCH₃)],¹⁵ and (iii) hydrazoic acid (HN₃).¹⁶ HN₃ is a desirable nitrogen source because it has the highest N:H ratio of all three. When it decomposes, HN₃ preferentially breaks the N–N single bond first, leaving an NH radical on the substrate surface which can easily react to form the nitride. The remaining nitrogen dimer may also remain adsorbed on the surface for possible nitride formation, but will more likely desorb and form N₂.¹⁰ Unfortunately, HN₃ is highly explosive when in a condensed phase,¹⁷ so its application as a nitrogen source has severe safety concerns.

Of the two remaining nitrogen sources, the N:H ratio of
N₂H₄ is 1:2 compared to the 1:3 ratio for NH₃. N₂H₄ is also more easily cracked than NH₃:\(^{17}\)

\[
\text{N}_2\text{H}_4 \rightarrow 2\text{NH}_2 + \text{e}, \quad \Delta H^\circ = 71 \text{ kcal/mol},
\]

\[
\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}, \quad \Delta H^\circ = 110 \text{ kcal/mol}.
\]

N₂H₄ can actually be used to form radicals at temperatures as low as 0 °C without the aid of a plasma.\(^{18}\) The cracking of N₂H₄ is facilitated by catalytic surfaces, onto which the molecule may adsorb either end on (-NH₂ adsorption) or side on (-NH₂ adsorption), depending upon the surface, coverage, and temperature.\(^{19-22}\) N₂H₄ adsorbs onto (100) GaAs surfaces side-on, and the decomposition products may include NH₃, N₂, or H₂, depending upon the GaAs surface temperature.\(^{19}\)

Some concerns have been expressed about the use of anhydrous liquid N₂H₄ because it is a carcinogen, highly flammable, and explosive under certain conditions.\(^{18}\) N₂H₄ has a melting point of 274.5 K, boiling point of 386.7 K, and vapor pressure of 1.92 kPa at 25 °C.\(^{18}\) necessitating the use of gaseous N₂H₄ at low pressures. In addition, the strong affinity of N₂H₄ for H₂O makes their separation below 0.1% difficult by traditional separation methods such as distillation and crystallization. The H₂O impurities in anhydrous liquid N₂H₄ have been of particular concern for nitride film growth because of the incorporation of oxides into the nitride film.\(^{16,17}\) Several methods have been developed for purifying N₂H₄, including drying anhydrous liquid N₂H₄ over molecular sieves\(^{23}\) and distilling anhydrous liquid N₂H₄ over NaOH and CuO.\(^{24}\) Nachbaur and Leiseder developed a method for purifying N₂H₄ in which N₂H₄ is bound to cyanuric acid (C₃H₃N₃O₃) (CA) in a solid complex, hydrazine cyanurate (C₃H₃N₃O₃N₂H₄) (HC).\(^{25}\)

In this article, a process has been developed for synthesizing HC with low H₂O content, and using the evolved N₂H₄ at low pressure to nitridate (100) GaAs. The N₂H₄ was analyzed by mass spectrometry (MS) and gas chromatography (GC), and the nitride films were analyzed by x-ray photoelectron spectroscopy (XPS).

II. EXPERIMENT

N₂H₄ is a flammable reducing agent, therefore contact with oxidizers should be avoided.\(^{18}\) For this reason, the anhydrous liquid N₂H₄ (Olin) was stored in a Vacuum Atmospheres inert atmosphere dry box which had H₂O and O₂ concentrations of less than 2 ppm. HC was synthesized in a three-neck, 1000 ml round bottom flask which was equipped with a heating jacket and was supported over a magnetic stirrer/hot plate. One neck of the flask held a thermometer; the second neck was stoppered and was used for the addition of reactants, and the third neck supported a condenser. The flask could be evacuated with a mechanical pump and purged with N₂ through the top of the condenser.

The preparation of HC began by adding 320 ml of deionized H₂O and 12.93 grams of CA (Fluka) to the round bottom flask which was kept under a N₂ atmosphere at all times. The contents of the flask were magnetically stirred while being heated to 100 °C. At 100 °C, 3.4 ml of anhydrous liquid N₂H₄ were transferred from the inert atmosphere dry box and were added to the flask. The molecular structures of CA and N₂H₄ are shown in Fig. 1. N₂H₄ reacted with the CA within seconds to form HC as a white precipitate. The HC crystals were then dried in a Buchner funnel, and excess solvent was poured into a 5% NaHClO aqueous solution to neutralize any residual N₂H₄. The solid HC was further vacuum dried at 120 °C and a pressure less than 10⁻³ Torr, after which it was stored in the inert atmosphere dry box. The synthesized HC had the appearance of fine white crystals. These crystals are only slightly soluble in H₂O and are toxic if inhaled, ingested, or contacted with skin.

Analysis of liquid H₂O and N₂H₄ was performed by GC/MS using a standard addition of 20 vol % H₂O in N₂H₄. A Hewlett-Packard 5890 GC was equipped with a 30 m DB-5 column which had a 0.25 mm i.d. and a 0.25 μm film thickness. The temperature of the GC was increased from 50 to 300 °C at a constant rate of 15 °C per minute. The gases exiting the GC column were immediately introduced into a VG Instruments 70-SE MS which was run in Selective Ion Recording mode for data acquisition. To analyze the N₂H₄ evolved from HC, a small sample of HC was first isolated in a capillary tube in the inert atmosphere dry box. The capillary tube was then sealed with wax to prevent contamination of the HC during transport to the MS. When ready for analysis, the top of the capillary tube was scored and removed. The bottom of the capillary tube contained the HC and was immediately introduced into the MS. The inlet temperature of the MS was 30 °C which was increased to a final temperature of 400 °C at a constant rate of 2 °C per second. Analysis of the gases evolved from HC was done by MS with the instrument operating in probe mode for data acquisition.

Figure 2 shows a schematic of the new low pressure chemical vapor deposition (LPCVD) reactor constructed to determine the feasibility of using HC as a nitrogen source for nitride film growth. The system was constructed with standard ultrahigh vacuum compatible components, including the glass-to-metal seal of the viewport and the ceramic-to-metal seals of the feedthroughs. The system was rough pumped by a liquid N₂ cooled Riber cryosorption pump, and the main pump was a Balzers turbopump which had a pumping speed.
of $56 / s^{-1}$. The system had both a Pirani and a cold cathode gauge to cover a pressure range of $10^2 - 10^{-9}$ Torr. After bakeout, the vacuum system had a base pressure of less than $10^{-6}$ Torr. A Spectra Instruments VacScan residual gas analyzer (RGA) with a range of 1–100 amu was used to monitor the vacuum gases. A butterfly valve isolated the RGA from the reaction chamber so that its filaments would not become excessively contaminated during the growth process. At higher pressures (above $10^{-4}$ Torr), the cryosorption pump could be used to differentially pump the RGA.

Substrates were loaded into the reactor with a vacuum pickup tool by removing the viewport. The HC cell was charged in the inert atmosphere dry box and kept under a N$_2$ blanket until the vacuum system was reassembled and evacuated. Butterfly valves were positioned so that the HC cell could be isolated and removed from the LPCVD reactor while it was charged. This step was taken to prevent contamination of the HC prior to growth.

The HC cell and the substrate heater were equipped with current and thermocouple feedthroughs which allowed for heating and precise temperature control of both the substrate and HC cell. The substrate heater was custom made from a 0.25 in. thick tantalum disc which was 3 in. in diameter. Five holes were tapped through the tantalum disc in a symmetric pattern, and threaded tantalum rod was used to connect ceramic standoffs to the tantalum disc. A tantalum wire, power supply, and feedthroughs were used as a substrate heater. A small hole was bored into the side of the tantalum disc into which a J-type thermocouple probe was inserted to measure the temperature at the center of the tantalum disc. This temperature was assumed to be roughly equal to the substrate temperature. The HC cell consisted of a pyrolytic boron nitride (PBN) evaporation crucible which was heated by a tungsten basket. The ends of the basket were silver soldered to the current leads of the feedthrough. A J-type thermocouple was used to measure the temperature of the contents of the PBN evaporation crucible in the HC cell.

The LPCVD reactor was first loaded with HC and a precleaned (100) n-type GaAs substrate doped at 1.0–1.2 x 10$^{17}$ cm$^{-3}$. The system was then evacuated and He leak checked with the RGA, and once certified to be leak free, the system was baked at 100 °C with the substrate at the 200 °C growth temperature. After bakeout, the reactor was cooled to room temperature. It has been shown that H$_2$ treatments of III-V semiconductor surfaces can deplete the Group V element, leaving a surface rich in the Group III element to facilitate the formation of the Ga–N bond. A H$_2$ treatment was carried out with the substrate at the growth temperature for a total hydrogen exposure of 0.28 L. Note that the reactor should be kept at room temperature or cooler during the H$_2$ treatment to prevent embrittlement of stainless steel components. After the H$_2$ treatment, the substrate was maintained at the 200 °C growth temperature while the HC cell was heated to 210 °C. Once the HC cell reached 200 °C, the right angle valve to the turbopump and valves 2 and 3 of Fig. 2 were closed so that the growth chamber would fill with N$_2$H$_4$ for the nitridation.

The nitridated GaAs surfaces were analyzed ex situ by XPS with a Surface Science SSX-100 ESCA spectrometer. Because the LPCVD reactor and the XPS were not connected, the nitride films were stored in a N$_2$ filled container during their transport from the LPCVD system to the XPS. The XPS spectra were recorded using Al Kα x-rays at a minimum energy resolution of 0.95 eV. The spectrometer was calibrated with the Au 4f$\gamma/2$ peak at 84.0 eV. Because the nitride films were so thin (roughly 10 Å), the films were not sputtered to remove surface contamination, and as a result, adventitious carbon and oxygen are present in the XPS spectra.

III. RESULTS

Mass spectra were taken of anhydrous liquid N$_2$H$_4$, liquid H$_2$O, and liquid N$_2$H$_4$ with a standard addition of 20 vol % H$_2$O to compare of the separation of H$_2$O from N$_2$H$_4$ in the solid complex versus the liquid phase mixture. Figure 3 shows the GC/MS chromatogram for the 20 vol % solution of H$_2$O in N$_2$H$_4$. The injection of the liquid sample into the GC occurred at 1:45, and the data was collected with the GC/MS detector tuned to the 17 amu signal. The large peak in the chromatogram at 2:15 min corresponds to NH$_3$, a de-
composition product of N₃H₄. A shoulder was observed at 3:30 corresponding to OH⁻, a decomposition product of H₂O. The overlap of these individual peaks demonstrates the difficulty of separating liquid H₂O from liquid N₃H₄.

MS was also used to determine the relative H₂O content of the gases evolved during heating of the HC so that the separation of H₂O from N₃H₄ could be verified. The MS analysis was performed by heating the HC to 200 °C at which point N₃H₄ gas was liberated and solid CA remained. If heated to 245 °C, the solid CA will further decompose into gaseous cyanic acid.²⁵ Figures 4(a) and 4(b) are MS data at 18 amu (H₂O) and 32 amu (N₃H₄), respectively, as a function of temperature for the HC produced by the original Nachbau and Leiseder process.²³ This sample was vacuum dried at 120 °C at less than 10⁻³ Torr for one hour. Evolved H₂O was observed at 100 °C and coevolved with N₃H₄ above 200 °C. The peak height of Fig. 4(a) (H₂O) at 240 °C is 1.4×10⁵ counts, while the peak height of Fig. 4(b) (N₃H₄) at 240 °C is 4.1×10⁶ counts. The H₂O signal is almost 10% of the total ion count at the peak of N₃H₄ evolution. H₂O impurities resulting from the use of H₂O as the solvent are a major disadvantage of the Nachbau and Leiseder process for producing HC.

Since lowering the H₂O impurity in N₃H₄ was a goal of this work, a polar organic solvent was selected for the synthesis of HC in place of H₂O. Several solvents were used to synthesize HC, including dimethylsulfoxide (DMSO), pyridine, ethanol (EtOH), and acetonitrile (MeCN). The HC produced in DMSO had the lowest H₂O impurity in the evolved N₃H₄, as measured by MS. Figures 5(a) and 5(b) are the 18 and 32 amu signals, respectively, for HC produced in DMSO. This sample was dried with a Buchner funnel, but not vacuum dried. The peak height of Fig. 5(a) (H₂O) at 120 °C is 3.0×10⁶ counts, while the peak height of Fig. 5(b) (N₃H₄) at 320 °C is 2.2×10⁷ counts. At 320 °C, the signal of Fig. 5(a) is 7.4×10⁵ counts, or only 1% of the total ion count at the peak of N₃H₄ evolution. This is an order of magnitude decrease in the H₂O content of the gases evolved from HC as compared to the HC synthesized by using H₂O as the solvent. A further evaluation of the purity of the HC synthesized in DMSO is seen in the onset of N₃H₄ evolution in Fig. 5 at over 200 °C compared to the onset of N₃H₄ evolution in Fig. 4 at under 200 °C. This difference is attributable to the H₂O impurities in the HC synthesized in H₂O disrupting the HC crystal structure and decreasing the temperature at which the N₃H₄ evolves. After vacuum drying the sample synthesized in DMSO at 120 °C and at less than 10⁻³ Torr for 72 h, the H₂O signal dropped to 0.7% of the total ion count. This demonstrates that N₃H₄ and H₂O can be separated when HC is synthesized in DMSO.

During the nitridation of (100) GaAs using N₃H₄ evolved from HC synthesized in DMSO, the gaseous species present in the LPCVD reactor were monitored with the RGA. This data is best interpreted by following the trends in the partial pressures of the gaseous species rather than focusing on the absolute numbers. Prior to N₃H₄ evolution, the background pressure of the vacuum system was 10⁻⁷ Torr, and no N₃H₄ evolution was observed. This indicates that the vapor pressure of HC is insignificant below its activation temperature. At the onset of N₃H₄ evolution, the 28 and 18 amu signals were the strongest at 2.5×10⁻⁶ and 1.5×10⁻⁶ Torr, respectively. These can be attributed to background N₂ (and to a lesser degree CO from filament outgassing) and H₂O. The 28 amu signal steadily increased at a rate of 1 μTorr/h, while the 18 amu signal decreased at a rate of 0.3 μTorr/h to a final pressure of 5.0×10⁻⁷ Torr. The 16 and 17 amu signals steadily increased at the rate of 0.3 μTorr/h to reach pressures of 1.0×10⁻⁶ Torr at the end of the growth. When the N₃H₄ products reach their peak pressures, the 18 amu signal accounted for about 9% of the total gaseous species in the reactor. It should be noted, however, that the 18 amu signal did not increase upon heating the HC. This would imply that the H₂O present in the system was residual gas from the bakeout, and a more thorough bakeout procedure should be used.
A noteworthy feature of the RGA data is the lack of a 32 amu signal (N$_3$H$_4$). This can be caused by N$_2$H$_4$ decomposition in the chamber and in the RGA detector. The heater filaments and pressure gauges in the system can easily catalyze the decomposition of N$_2$H$_4$, and therefore, the decomposition products of N$_2$H$_4$ were used to trace the presence of N$_2$H$_4$. These decomposition products include N$_2$ (28 amu) and NH$_3$ (17 amu), which is the most common decomposition product of N$_2$H$_4$ at these temperatures. Other fragments were also present in lesser quantities; N (14 amu), NH (15 amu), and NH$_2$ (16 amu). Unfortunately, both the 16 and 17 amu signals are ambiguous because they can be from either H$_2$O or N$_2$H$_4$. Therefore, ratios of these species relative to the parent signal of H$_2$O (18 amu) were used to interpret the data.

The ratio of 17:18 amu five minutes after the onset of N$_2$H$_4$ evolution was 70:100. A significant amount of the 17 amu signal was attributable to NH$_3$ because the characteristic ratio of the 16:17:18 amu signals in the cracking pattern of H$_2$O is 1:20:100. The 17 amu signal was equal to the 18 amu signal at 7.0 x 10$^{-7}$ Torr after 40 min. The 16:17 ratio in the cracking pattern of NH$_3$ was 80:100 and was experimentally observed to be 83:100. In addition, the fact that the 16 amu signal follows the same pattern of the 17 amu signal indicates that the 16 amu signal is attributable, in large part, to NH$_2$.

The nitridated GaAs wafers were mirrorlike when removed from the LPCVD system, and the nitridated surfaces appeared to be featureless when viewed with an optical microscope at 750X. An XPS survey was taken of the nitridated GaAs surfaces, and is shown in Fig. 6. Adventitious carbon and oxygen were present on the sample due to transfer in air. Sputter cleaning was not used because it could alter the nitride signal. The strong As 3p$_{3/2}$ peak at 140 eV would indicate that the surface conversion of the arsenide to the nitride was incomplete. This may be due to several factors, including an insufficient N$_2$H$_4$ flux to the surface or insufficient Group V element depletion during the H$_2$ pretreatment.

FIG. 6. A general XPS spectrum of a (100) GaAs surface nitridated at 200°C by N$_2$H$_4$ evolved from HC synthesized in DMSO. Note that the peak labels correspond to the peak directly beneath the element symbol.

The N$_2$H$_4$ flux could be increased by increasing the HC charge at the beginning of the growth, or the reactor could also be reconfigured to put the substrate in the direct pathway of the evolving N$_2$H$_4$. The N 1s peak expected at 398 eV was obscured by the broad Ga Auger peak at 393 eV, so a high resolution spectrum of the region from 390–410 eV was taken such that the N 1s peak could be examined. The Ga Auger peak appears at 393 eV, and the N 1s peak was detectable at 399 eV. The absence of N 1s peaks at energies greater than 400 eV shows that the film was a nitride and not a nitrite, nitrate, or oxynitride. Shown in Fig. 7 is a high resolution spectrum of the Ga 3d peak. Notable features of Fig. 7 are (i) the large peak at 19.53 eV due to GaN, (ii) the shoulder on the right of this peak due to the presence of GaAs, and (iii) the broad Ga$_2$O$_3$ shoulder at 20.94 eV. This spectrum confirms the incomplete conversion of the surface from an arsenide to a nitride. It also shows that significant Ga$_2$O$_3$ impurities are on the surface. The source of these oxides and their removal will be discussed in the next section.

IV. DISCUSSION

A solid source of N$_2$H$_4$ has been developed which is stable at low pressures, and can be vacuum baked to improve purity. The HC adduct is most likely formed through hydrogen bonding with the electronegative nitrogen atoms of the CA molecule. Refer to Fig. 1 for the structures of CA and N$_2$H$_4$. N$_2$H$_4$ has two pairs of hydrogen atoms which can form bridges between the CA molecules, leading to the regular, repeating crystal structure of HC. H$_2$O does not form these bridging structures because it has only one pair of hydrogen atoms. However, it would seem likely that a cyano acid hydrate does form. Such a hydrate species may be the source of the large H$_2$O signal coincident with N$_2$H$_4$ evolution in Fig. 4.

The MS data indicate that the HC samples synthesized in some solvents retained H$_2$O better than others. All of the polar solvents used in the synthesis of HC have some H$_2$O impurities, but those which also hydrogen bond seem to have a higher affinity for H$_2$O. In the solvents which strongly hydrogen bonded with H$_2$O, more of the cyano acid hy-
drate seemed to form. This was clear in the case of EtOH and MeCN. Both of these HC samples had H₂O concentrations of 1.7% at the peak of N₂H₄ evolution, more than twice that of the samples synthesized in DMSO. Because DMSO is a bulky molecule, steric effects may hinder the formation of hydrogen bonds with H₂O. Hence, less cyanuric acid hydrate would be formed and purer N₂H₄ can be evolved from the HC synthesized in DMSO.

It is speculated that the following two reactions (along with many others) are important in the nitridation process:

\[ 4\text{GaAs}_s + 3\text{N}_2\text{H}_4(g) \rightarrow 4\text{GaN}_s + 4\text{AsH}_3(g) + \text{N}_2(g), \]
\[ \Delta G^\circ = -375.0 \text{ kJ/mol,} \]
\[ 2\text{GaAs}_s + 6\text{H}_2\text{O}(g) \rightarrow \text{GaO}_3\text{S}_6 + 3\text{As}_2\text{O}_3\text{S}_6 + 6\text{H}_2(g), \]
\[ \Delta G^\circ = -55.1 \text{ kJ/mol.} \]

These reactions were chosen to be representative of the competition between nitridation and oxidation of the GaAs substrate. According to standard Gibbs Energy changes, both reactions are thermodynamically favorable. It is generally known, however, that oxidation is a relatively slow process, so the oxides will probably not grow at the same rate as the nitrides.

As a comparison, the nitride films produced in this study were compared to (100) GaAs surfaces nitridated at 400 °C and atmospheric pressure using liquid N₂H₄ as the nitrogen source. In the previous study, the ratio of constituent peak heights in the Ga 3d peak of GaN to GaO was 4.8, while in our films grown at 200 °C and low pressure the ratio of the peak heights is 2.25. A major reason for the difference is that thicker films are formed at higher growth temperatures. Therefore, the nitrogen content of the films reported here is lower. The oxygen content of the films has a large effect on this ratio. The films grown at atmospheric pressure were pre-cleaned and grown in an inert atmosphere drybox, which significantly reduced the amount of oxide impurities grown prior to the growth of the nitride films. The major source of the oxide impurities in these films was H₂O impurity in the liquid N₂H₄, as demonstrated in Fig. 3. The substrates used in this article were not cleaned in an inert atmosphere drybox and experienced significant exposure to the atmosphere before being loaded into the LPCVD system. Because it has been demonstrated that the HC source used for this nitride film growth has lower H₂O impurities, the oxide impurities in these nitride films are most likely due to an incomplete removal of the native substrate oxide prior to growth.

**V. CONCLUSIONS**

HC was used as a nitrogen source for nitride film growth, with particular attention paid to the solvent used for the synthesis of HC. H₂O was replaced with DMSO in the synthesis of HC, and this was found to reduce the H₂O content of the N₂H₄ gas evolved upon heating of the HC. The HC synthesized in DMSO was then used in an LPCVD reactor to nitridate the surfaces of (100) GaAs substrates. The grown nitride films were analyzed by XPS and were found to be composed primarily of GaN and GaAs with some Ga₂O₃ impurities. These impurities were most likely not a result of using HC as the nitrogen source, but from the incomplete removal of the surface oxide prior to growth. N₂H₄ gas evolved from HC is therefore an effective source of active nitrogen for nitridation reactions. Future work includes characterization of the HC source, elimination of the oxides in the resulting nitride films, and a comparison of this source to other widely used nitridation techniques like NH₃ and plasma nitridations.

**ACKNOWLEDGMENTS**

This work was supported under AFOSR Grant F49620-95-1-0527. The authors wish to thank Dr. Anis Husain of DARPA and Dr. Gerald Witt of AFOSR. We would also like to thank Dave Bostwick for obtaining the mass spectra, Dr. Frank Stepniak for help in designing the LPCVD reactor, Dr. Alan Doolittle for help in overcoming some technical issues which arose during the implementation of the LPCVD reactor, and Dr. W. Brent Carter for XPS expertise.

2CRC Handbook of Chemistry and Physics (CRC, Boca Raton, FL, 1993).