

Hydrazine cyanurate as a nitrogen source for thin nitride film growth

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The use of liquid hydrazine (N_2H_4) 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 N_2H_4 which can be easily handled and purified before use and which evolves pure N_2H_4 upon heating, thus making it a promising source of N_2H_4 for nitridation reactions. In this article, a process for the synthesis of HC has been developed which decreases the H_2O content of the evolved N_2H_4 from 10% when H_2O was used as the solvent in the synthesis of HC to 0.7% by replacing H_2O 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 Ga_2O_3 . The ratio of the constituent peak heights in the Ga 3d peak of GaN to Ga_2O_3 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 Si_3N_4 is a useful dielectric material in Si integrated circuits because it has a higher dielectric constant ($\epsilon=5.5\text{--}9.4$) than SiO_2 ($\epsilon=3.8$).¹ Si_3N_4 is also denser ($\rho=3.4\text{ g/cm}^3$) than SiO_2 ($\rho=2.2\text{--}2.6\text{ g/cm}^3$)² and thus is a better diffusion barrier to impurities.¹ Thin films of TiN_x and WN_x 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.⁵

Wide band gap semiconductors with direct transitions are of interest because of their use in blue light emitting diodes and high temperature electronic devices.⁶ The Group III nitride semiconductors, which include AlN ($E_g=6.2\text{ eV}$), GaN ($E_g=3.4\text{ eV}$), InN ($E_g=1.9\text{ eV}$), 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%.^{7,8} 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 N_2 is problematic because of its stability and bond strength ($\Delta H^\circ=946\text{ kJ/mol}$).⁹ Surface nitrogen atoms can easily desorb as N_2 , 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 N_2 . The high activation energy for N_2 requires high temperatures or plasma activation;¹⁰ however, high energy particles created in rf and electron cyclotron resonance plasmas can damage semiconductor surfaces,^{11–13} and final device performance may suffer.¹⁴ Thus, alternate sources of active nitrogen species may be a critical enabling technology for nitride growth.

An alternative to activating N_2 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 (NH_3),¹⁵ (ii) hydrazine (N_2H_4)^{15,16} and its organic derivatives [e.g., monomethylhydrazine (NH_2NHCH_3)],¹⁴ and (iii) hydrazoic acid (HN_3).¹⁰ HN_3 is a desirable nitrogen source because it has the highest N:H ratio of all three. When it decomposes, HN_3 preferentially breaks the N–N single bond first, leaving an $\bullet\text{NH}$ 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 N_2 .¹⁰ Unfortunately, HN_3 is highly explosive when in a condensed phase,¹⁰ so its application as a nitrogen source has severe safety concerns.

Of the two remaining nitrogen sources, the N:H ratio of

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N_2H_4 is 1:2 compared to the 1:3 ratio for NH_3 . N_2H_4 is also more easily cracked than NH_3 :¹⁷



N_2H_4 can actually be used to form radicals at temperatures as low as 0 °C without the aid of a plasma.¹⁸ The cracking of N_2H_4 is facilitated by catalytic surfaces, onto which the molecule may adsorb either end on ($-\text{NH}$ absorption) or side on ($-\text{NH}_2$ adsorption), depending upon the surface, coverage, and temperature.^{19–22} N_2H_4 adsorbs onto (100) GaAs surfaces side-on, and the decomposition products may include NH_3 , N_2 , or H_2 , depending upon the GaAs surface temperature.¹⁹

Some concerns have been expressed about the use of anhydrous liquid N_2H_4 because it is a carcinogen, highly flammable, and explosive under certain conditions.¹⁸ N_2H_4 has a melting point of 274.5 K, boiling point of 386.7 K, and vapor pressure of 1.92 kPa at 25 °C,^{2,18} necessitating the use of gaseous N_2H_4 at low pressures. In addition, the strong affinity of N_2H_4 for H_2O makes their separation below 0.1% difficult by traditional separation methods such as distillation and crystallization. The H_2O impurities in anhydrous liquid N_2H_4 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 N_2H_4 , including drying anhydrous liquid N_2H_4 over molecular sieves²³ and distilling anhydrous liquid N_2H_4 over NaOH and CaO.²⁴ Nachbaur and Leiseder developed a method for purifying N_2H_4 in which N_2H_4 is bound to cyanuric acid ($\text{C}_3\text{H}_3\text{N}_3\text{O}_3$) (CA) in a solid complex, hydrazine cyanurate ($\text{C}_3\text{H}_3\text{N}_3\text{O}_3 \cdot \text{N}_2\text{H}_4$) (HC).²⁵

In this article, a process has been developed for synthesizing HC with low H_2O content, and using the evolved N_2H_4 at low pressure to nitridate (100) GaAs. The N_2H_4 was analyzed by mass spectrometry (MS) and gas chromatography (GC), and the nitride films were analyzed by x-ray photoelectron spectroscopy (XPS).

II. EXPERIMENT

N_2H_4 is a flammable reducing agent, therefore contact with oxidizers should be avoided.¹⁸ For this reason, the anhydrous liquid N_2H_4 (Olin) was stored in a Vacuum Atmospheres inert atmosphere dry box which had H_2O and O_2 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 N_2 through the top of the condenser.

The preparation of HC began by adding 320 ml of deionized H_2O and 12.93 grams of CA (Fluka) to the round bottom flask which was kept under a N_2 atmosphere at all times. The contents of the flask were magnetically stirred

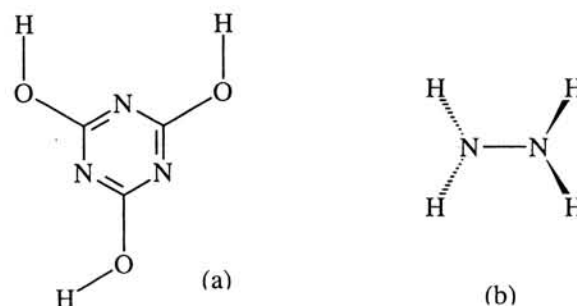


Fig. 1. The structures of the (a) cyanuric acid and (b) hydrazine molecules.

while being heated to 100 °C. At 100 °C, 3.4 ml of anhydrous liquid N_2H_4 were transferred from the inert atmosphere dry box and were added to the flask. The molecular structures of CA and N_2H_4 are shown in Fig. 1. N_2H_4 reacted with the CA within seconds to form HC as a white precipitate. The HC crystals were first dried in a Buchner funnel, and excess solvent was poured into a 5% NaHClO aqueous solution to neutralize any residual N_2H_4 . 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 H_2O and are toxic if inhaled, ingested, or contacted with skin.

Analysis of liquid H_2O and N_2H_4 was performed by GC/MS using a standard addition of 20 vol % H_2O in N_2H_4 . 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 N_2H_4 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 N_2 cooled Riber cryosorption pump, and the main pump was a Balzers turbopump which had a pumping speed

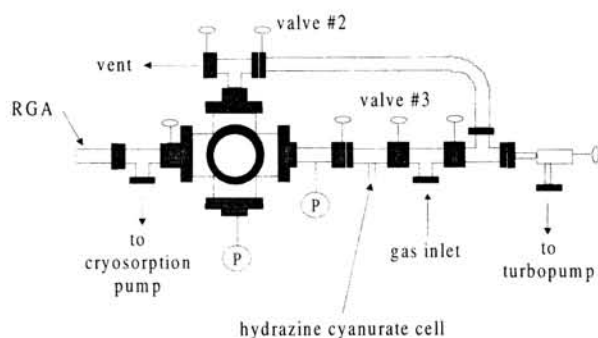


FIG. 2. A schematic of the LPCVD reactor used for nitridation reactions with N_2H_4 gas evolved from HC as the nitrogen source.

of $56/\text{s}^{-1}$. 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 pre-cleaned (100) *n*-type GaAs substrate doped at 1.0 – $1.2 \times 10^{17} \text{ cm}^{-3}$. 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

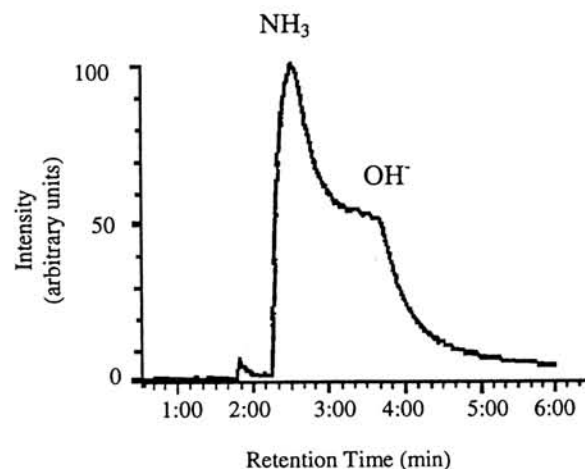


FIG. 3. A GC/MS chromatogram of a 20 vol % solution of H_2O in N_2H_4 .

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.^{16,26} 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_2H_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 $K\alpha$ x-rays at a minimum energy resolution of 0.95 eV. The spectrometer was calibrated with the Au $4f_{7/2}$ 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_2H_4 , liquid H_2O , and liquid N_2H_4 with a standard addition of 20 vol % H_2O to compare of the separation of H_2O from N_2H_4 in the solid complex versus the liquid phase mixture. Figure 3 shows the GC/MS chromatogram for the 20 vol % solution of H_2O in N_2H_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-

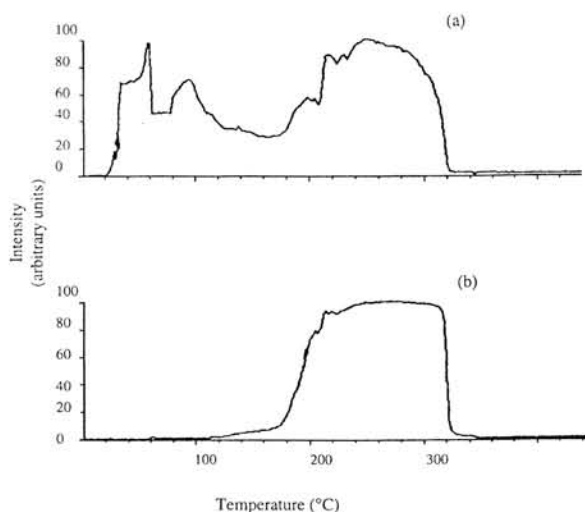


Fig. 4. MS of 18 amu signal (a) and 32 amu signal (b) for HC produced in H_2O .

composition product of N_2H_4 . A shoulder was observed at 3:30 corresponding to OH^- , a decomposition product of H_2O . The overlap of these individual peaks demonstrates the difficulty of separating liquid H_2O from liquid N_2H_4 .

MS was also used to determine the relative H_2O content of the gases evolved during heating of the HC so that the separation of H_2O from N_2H_4 could be verified. The MS analysis was performed by heating the HC to 200 °C at which point N_2H_4 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 (H_2O) and 32 amu (N_2H_4), respectively, as a function of temperature for the HC produced by the original Nachbaur and Leiseder process.²⁵ This sample was vacuum dried at 120 °C at less than 10^{-3} Torr for one hour. Evolved H_2O was observed at 100 °C and coevolved with N_2H_4 above 200 °C. The peak height of Fig. 4(a) (H_2O) at 240 °C is 1.4×10^7 counts, while the peak height of Fig. 4(b) (N_2H_4) at 240 °C is 4.1×10^8 counts. The H_2O signal is almost 10% of the total ion count at the peak of N_2H_4 evolution. H_2O impurities resulting from the use of H_2O as the solvent are a major disadvantage of the Nachbaur and Leiseder process for producing HC.

Since lowering the H_2O impurity in N_2H_4 was a goal of this work, a polar organic solvent was selected for the synthesis of HC in place of H_2O . Several solvents were used to synthesize HC, including dimethylsulfoxide (DMSO), pyridine, ethanol (EtOH), and acetonitrile (MeCN). The HC produced in DMSO had the lowest H_2O impurity in the evolved N_2H_4 , 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) (H_2O) at 120 °C is 3.0×10^6 counts, while the peak height of Fig. 5(b) (N_2H_4) at 320 °C is 2.2×10^7 counts. At 320 °C, the signal of Fig. 5(a) is 7.4×10^5 counts, or only 1% of the total ion

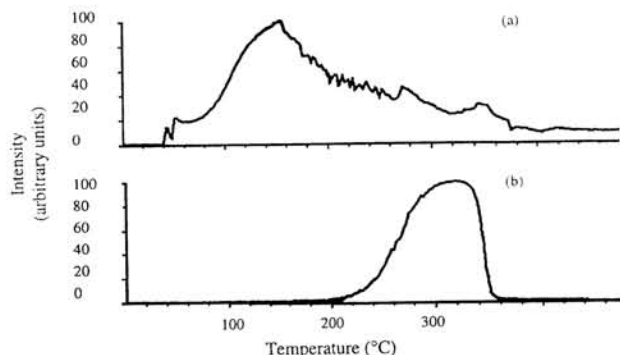


Fig. 5. MS of 18 amu signal (a) and 32 amu signal (b) for HC produced in DMSO.

count at the peak of N_2H_4 evolution. This is an order of magnitude decrease in the H_2O content of the gases evolved from HC as compared to the HC synthesized by using H_2O as the solvent. A further evaluation of the purity of the HC synthesized in DMSO is seen in the onset of N_2H_4 evolution in Fig. 5 at over 200 °C compared to the onset of N_2H_4 evolution in Fig. 4 at under 200 °C. This difference is attributable to the H_2O impurities in the HC synthesized in H_2O disrupting the HC crystal structure and decreasing the temperature at which the N_2H_4 evolves. After vacuum drying the sample synthesized in DMSO at 120 °C and at less than 10^{-3} Torr for 72 h, the H_2O signal dropped to 0.7% of the total ion count. This demonstrates that N_2H_4 and H_2O can be separated when HC is synthesized in DMSO.

During the nitridation of (100) GaAs using N_2H_4 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 N_2H_4 evolution, the background pressure of the vacuum system was 10^{-7} Torr, and no N_2H_4 evolution was observed. This indicates that the vapor pressure of HC is insignificant below its activation temperature. At the onset of N_2H_4 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 N_2 (and to a lesser degree CO from filament outgassing) and H_2O . The 28 amu signal steadily increased at a rate of $1 \mu\text{Torr/h}$, while the 18 amu signal decreased at a rate of $0.3 \mu\text{Torr/h}$ to a final pressure of 5.0×10^{-7} Torr. The 16 and 17 amu signals steadily increased at the rate of $0.3 \mu\text{Torr/h}$ to reach pressures of 1.0×10^{-6} Torr at the end of the growth. When the N_2H_4 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 H_2O present in the system was residual gas from the bakeout, and a more thorough bakeout procedure should be used.

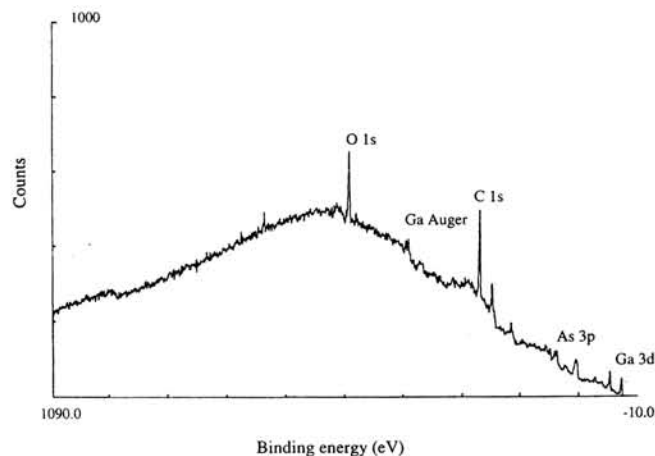


FIG. 6. A general XPS spectrum of a (100) GaAs surface nitridated at 200 °C by N_2H_4 evolved from HC synthesized in DMSO. Note that the peak labels correspond to the peak directly beneath the element symbol.

A noteworthy feature of the RGA data is the lack of a 32 amu signal (N_2H_4). This can be caused by N_2H_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_2H_4 , and therefore, the decomposition products of N_2H_4 were used to trace the presence of N_2H_4 . These decomposition products include N_2 (28 amu) and NH_3 (17 amu), which is the most common decomposition product of N_2H_4 at these temperatures.²⁰ 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_2O or N_2H_4 . Therefore, ratios of these species relative to the parent signal of H_2O (18 amu) were used to interpret the data.

The ratio of 17:18 amu five minutes after the onset of N_2H_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_2O is 1:20:100. The 17 amu signal was equal to the 18 amu signal at 7.0×10^{-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 750 \times . 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_2H_4 flux to the surface or insufficient Group V element depletion during the H_2 pretreatment.

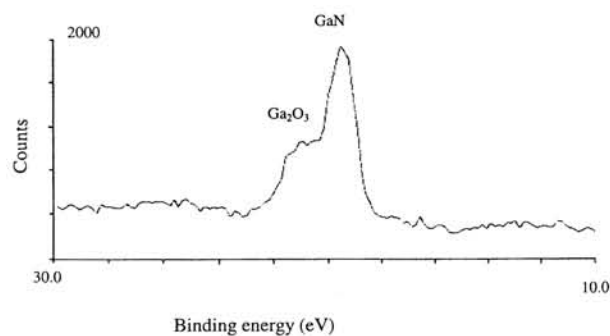


FIG. 7. A high resolution XPS spectrum of the Ga 3d peak of a (100) GaAs surface nitridated at 200 °C by N_2H_4 evolved from HC synthesized in DMSO.

The N_2H_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_2H_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 so 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_2O_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_2O_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_2H_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_2H_4 . N_2H_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_2O does not form these bridging structures because it has only one pair of hydrogen atoms. However, it would seem likely that a cyanuric acid hydrate does form. Such a hydrate species may be the source of the large H_2O signal coincident with N_2H_4 evolution in Fig. 4.

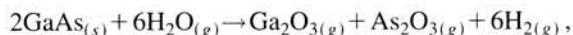
The MS data indicate that the HC samples synthesized in some solvents retained H_2O better than others. All of the polar solvents used in the synthesis of HC have some H_2O impurities, but those which also hydrogen bond seem to have a higher affinity for H_2O . In the solvents which strongly hydrogen bonded with H_2O , more of the cyanuric acid hy-

hydrate 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:



$$\Delta G^\circ = -375.0 \text{ kJ/mol},$$



$$\Delta G^\circ = -55.1 \text{ kJ/mol}.$$

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.¹⁶ In the previous study, the ratio of constituent peak heights in the Ga 3d peak of GaN to Ga₂O₃ is 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.¹⁶ The major source of the oxide impurities in these films was the H₂O impurity in the liquid N₂H₄,¹⁶ 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 nitride 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.

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