Hydrazine adsorption and decomposition on the GaAs(100)-c(8 × 2) surface

Elizabeth Apen [*,1], John L. Gland

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, USA

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Abstract

Temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and high resolution electron energy loss spectroscopy (HREELS) have been used to study the decomposition mechanism of hydrazine (N_2H_4) on the GaAs(100)-c(8 × 2) surface. Hydrazine adsorbs in a "side on" manner as indicated by XPS results. For small doses, hydrazine decomposition is complete, and the major decomposition product is ammonia, with nitrogen and hydrogen also being formed. For large doses, nitrogen is the major gas phase decomposition product. The absence of a high temperature atomic nitrogen recombination TPD peak indicates that nitrogen is made through an intramolecular mechanism. Both N_2H_y and NH_x species ($y = 1, 2, 3$; $x = 1, 2$) are identified as reaction intermediates. Above 350 K, only NH_x species are present on the surface.

1. Introduction

As the trend in device fabrication goes from micro- to nanoscale, the ability to characterize surface reactions on a molecular level is growing in importance. The use of GaAs based technology as a replacement for the traditional silicon/silicon dioxide based devices provides a path to devices which are faster and require less power for operation. The investigation of nitride layers as an alternative to insulating oxide layers has become more prevalent in the GaAs system. Gallium nitride has fewer interface trap states than the native oxide of GaAs, resulting in

better device performance. Nitride films have been grown on GaAs using nitrogen atoms [1,2], ammonia [3–6], and hydrazine [7–10]. Hydrazine is the focus of this work. Because of its high reactivity relative to nitrogen and ammonia, hydrazine should provide a low temperature pathway to high purity nitride films on GaAs. Hydrazine has been used in the chemical vapor deposition (CVD) growth of gallium nitride [7–10]. Researchers [7,8] have found that a hydrazine pretreatment of the GaAs surface before CVD growth results in the deposition of cubic (versus hexagonal) GaN films. Similar results have been found using dimethyl hydrazine [11]. A molecular understanding of the reaction of hydrazine with the GaAs surface is a necessary step in optimizing the conditions used for device fabrication.

The GaAs(100)-c(8 × 2) surface, the most gallium-rich surface reconstruction [12,13], has been used to study the decomposition mechanism of hy-

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[*] Corresponding author. E-mail: eapen@lanl.gov; Fax: + 1 505 667 8109.
[1] Present address: Chemical Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

drazine as a function of temperature and coverage. Temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and high resolution electron energy loss spectroscopy (HREELS) have been utilized to determine the intermediates of the decomposition reaction.

2. Experimental

The experiments were performed in an ultra-high vacuum chamber with a base pressure of 1×10^{-10} Torr. The chamber is equipped with temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and high resolution electron energy loss spectroscopy (HREELS). Sputtering, low energy electron diffraction (LEED), and Auger electron spectroscopy (AES) are also available.

The samples were 15 mm by 10 mm slices of n-doped GaAs(100) wafers. To resistively heat the sample, 3000 Å of Ta was sputter deposited onto the back of the wafer, which was then sliced into sample-sized pieces. The samples were mounted via two Ta clips onto a liquid nitrogen cooled manipulator. The manipulator is capable of 360° rotation to allow the sample to be placed directly in front of all detectors. The temperature was monitored by a chromel–alumel thermocouple which was spot-welded to a third Ta clip, which was press-fitted to the top of the GaAs sample between the two heating clips. To obtain a clean, ordered surface, the sample was treated using sputter and anneal cycles. A fifteen minute high temperature (733 K) argon ion sputter treatment was followed by a fifteen minute 773 K anneal and flash to 875 K. This provided a clean ordered GaAs(100)-c(8 × 2) surface as observed by LEED and AES.

Hydrazine was introduced into the chamber through a glass and polymer based gas inlet system which has been described elsewhere [14]. The advantage of this new inlet system is that no metal parts are used in the doser or gas lines. As a result, there is no decomposition of the hydrazine gas before introduction into the vacuum chamber as is common with metal-based inlet systems [14].

The ramp rate for all TPD experiments was 6 K/s. A reproducible linear heating ramp was provided by an analog voltage ramp generator. The voltage generator eliminated problems associated from the feedback loop in the traditional digital temperature controller and provided a linear heating rate over the 180 to 700 K temperature range. A multiplexed mass spectrometer was used to monitor up to ten desorbing species during one experiment. To minimize signal contributions from the Ta clips, the sample was placed approximately 1 mm away from the mass spectrometer collimator during the heating cycle. XPS data were collected using a standard hemispherical analyzer with $\text{Mg K}\alpha$ incident radiation. Typical data collection time for the N 1s region was 30 min with a pass energy of 22 eV. In order to remove contributions from the GaAs Auger background, the N 1s spectra from the clean GaAs(100)-c(8 × 2) surface has been subtracted from all N 1s XPS spectra below. A secondary electron background has also been subtracted in the form of a smoothed step function [15]. The XPS energy scale was referenced to the Ga 3d levels for bulk GaAs. HREELS spectra were taken at 130 K and a 0.6 eV/min scan rate. The resolution of the spectrometer varied from 95 to 100 cm^{-1}.

3. Results and discussion

3.1. Temperature programmed desorption (TPD)

Hydrazine adsorption on the GaAs(100)-c(8 × 2) surface results in four gas phase desorption products: H_2, NH_3, N_2, and N_2H_4. Fig. 1 shows the TPD spectra for these gas phase products after a 60 s exposure of hydrazine on the clean GaAs(100)-c(8 × 2) surface at 130 K. TPD yields of nitrogen and ammonia from 140 to 700 K as a function of hydrazine exposure are shown in Fig. 2. The TPD yields have been adjusted for the fragmentation of hydrazine in the mass spectrometer ionization chamber. Ammonia is the major channel for N desorption for small doses, while nitrogen is the major gas phase decomposition product at high exposure. This result implies that at low coverage, N–N bond breaking is favored, while at high coverage N–H bond breaking is favored. The largest exposure in Fig. 2 is on the order of one monolayer of surface coverage. All products (Fig. 1) have a desorption maxima in the 230–250 K temperature range. N_2, H_2, and NH_3

have a second desorption peak in the 300–700 K temperature range. Above 750 K, the nitrogen and hydrogen spectra have a desorption tail which increases in intensity to 900 K (not shown), the maximum substrate temperature. This high temperature tail was not observed for ammonia decomposition on this same surface using the same sample holder [16]. We believe the tail could be due to a combination of two factors: (1) a small contribution from the Ta sample holder, and (2) the desorption of nitrogen and hydrogen which have migrated into the subsurface during the earlier stages of the experiment. This phenomenon of nitrogen and hydrogen migration into the subsurface was not seen with ammonia decomposition, mainly because of the small amount of decomposition on the GaAs(100)-c(8 × 2) surface. TPD experiments were performed in which hydrazine was dosed directly onto the Ta sample holder and the holder was subsequently placed directly in

Fig. 2. TPD yield curves for nitrogen and ammonia desorption from hydrazine decomposition from 140 to 700 K on the GaAs(100)-c(8 × 2) surface. The yields have been adjusted for the fragmentation of the hydrazine in the mass spectrometer ionization chamber.
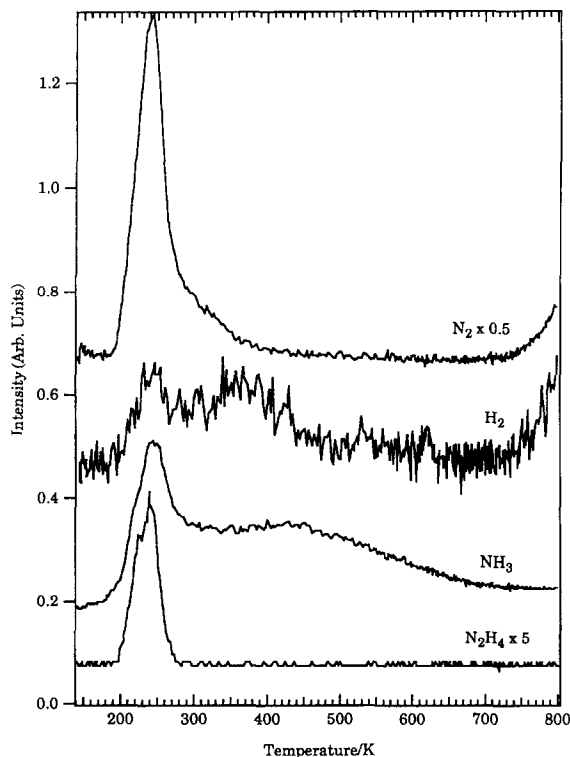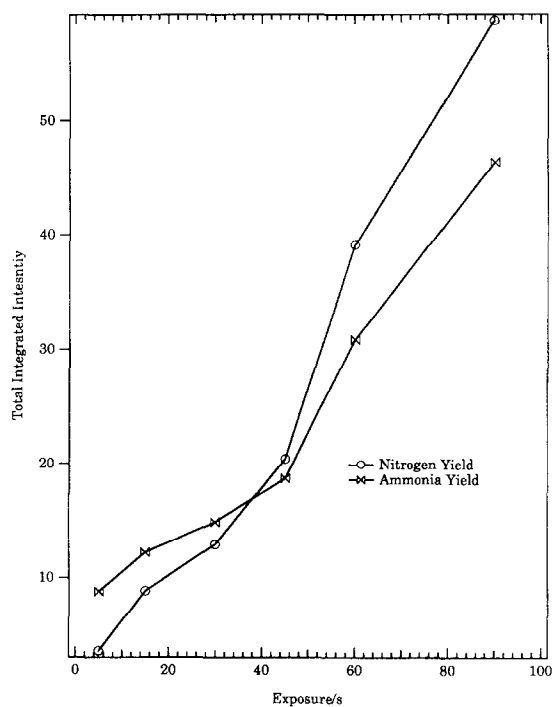

Fig. 1. Temperature programmed desorption spectra for all products of hydrazine decomposition on the GaAs(100)-c(8 × 2) surface. Exposure = 60 s, heating rate = 6 K/s.

front of the mass spectrometer for detection of desorbing products. Only a small increase in intensity ($< 10\%$) of the desorbing species was observed. From this information coupled with the ammonia data, we believe that desorption from the Ta sample holder cannot account for all of the high temperature desorption of N_2 and H_2.

An exposure set for hydrazine desorption is shown in Fig. 3. For small doses (5 s), decomposition on the GaAs(100)-c(8 × 2) surface is complete, with no parent (mass 32) detected by the mass spectrometer. Upon increasing the exposure, a desorption peak is observed at 250 K. At high exposures, the peak maximum shifts to 230 K. The 250 K peak is attributed to recombination of N_2H_y ($y = 1, 2, 3$; most likely N_2H_3) with H(ad) to form hydrazine, which has been observed on Pt(111) [17]. With increasing exposure, the monolayer is being com-

pleted, shifting the peak maximum to lower temperature. Monolayer desorption of hydrazine has been observed on Pt(111) at 205 K [17] and on Rh(100) at 220 K [18]. The multilayer desorption temperature for hydrazine has been reported between 170 and 180 K on polycrystalline Rh [19], Pt(111) [17], and Ni(111) [20].

Ammonia desorption from the GaAs(100)-c(8 × 2) surface for various hydrazine exposures is shown in Fig. 4. At all exposures, two desorption peaks are observed. For low exposures, the peaks are centered at 250 and 450 K, while at high exposures, the peaks shift to 240 and 425 K, respectively. The shift to lower temperature of the 250 K peak is a result of the growth of the hydrazine monolayer. Both the 250 and 450 K peak temperatures are above the molecular ammonia desorption temperature for the GaAs(100)-c(8 × 2) surface. In a previous study of ammonia adsorption on this surface, chemisorbed
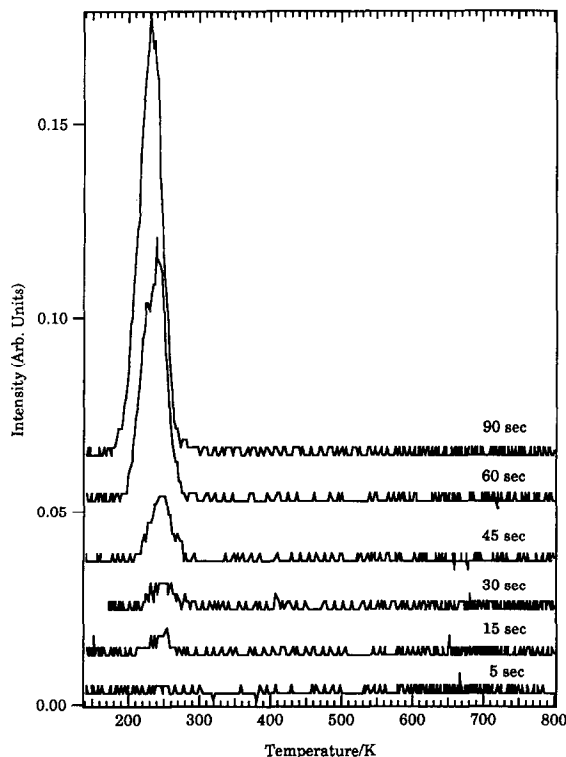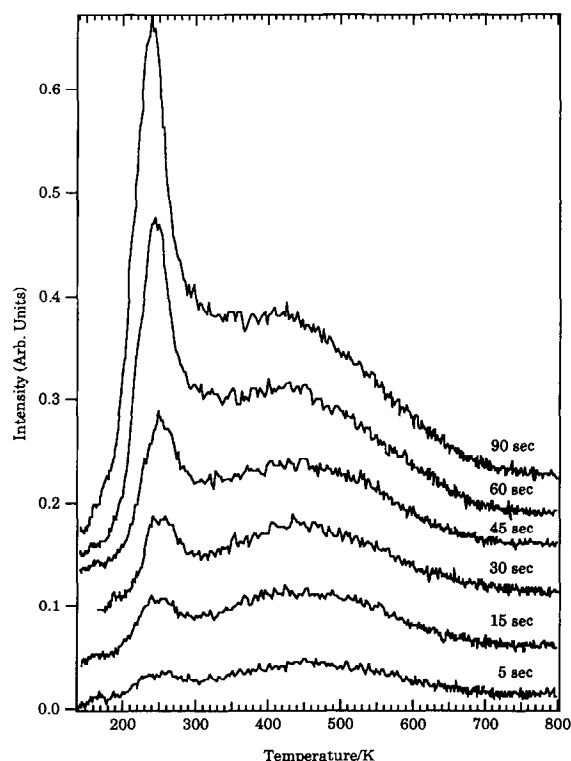

Fig. 4. Ammonia desorption from hydrazine decomposition on the GaAs(100)-c(8 × 2) surface at various exposures. Heating rate = 6 K/s.

ammonia was given off at 215 K and physisorbed ammonia at 160 K [16].

Fig. 5 presents the nitrogen desorption exposure set for hydrazine decomposition on GaAs(100)-c(8 × 2). For small exposures, a single peak at 260 K is observed. Increasing the dosage shifts this peak to 240 K and a shoulder at 325 K becomes evident. The shift to lower temperature of the 240 K peak is due to the growth of a hydrazine monolayer, mirroring the ammonia data in this temperature range. For large doses, nitrogen is the major desorption product, indicating that N–H bonds are broken preferentially upon adsorption at high coverage. Also supporting this conclusion is the absence of a high temperature desorption peak, typical of atomic nitrogen recombination. If N–N bonds were broken preferentially, some atomic nitrogen recombination should occur. Molecular nitrogen desorption from hydrazine decomposition has been observed at 800 K on Ni(111)

Fig. 3. Hydrazine desorption from hydrazine decomposition on the GaAs(100)-c(8 × 2) surface at various exposures. Heating rate = 6 K/s.

[20] and 950 K on polycrystalline Ir [21]. The absence of the atomic nitrogen recombination peak indicates that molecular nitrogen is made by some mechanism other than N atom recombination.

Hydrogen desorption from hydrazine decomposition on GaAs(100)-c(8 × 2) is shown in Fig. 6. For small doses, H_2 is given off at 230 and 370 K. With increasing exposure, the low temperature desorption peak shifts to 250 K, while the high temperature peak remains at 370 K.

TPD results show that at low exposure (5 s), hydrazine decomposition is complete, with ammonia as the major nitrogen containing desorption product at all temperatures. This implies that N–N bond breaking at these low exposures is favored over N–H bond cleavage. Upon increasing the exposure, a desorption peak for hydrazine recombination of N_2H_y + H(ad) is observed. For high exposure, nitrogen is the major decomposition product. Since no high
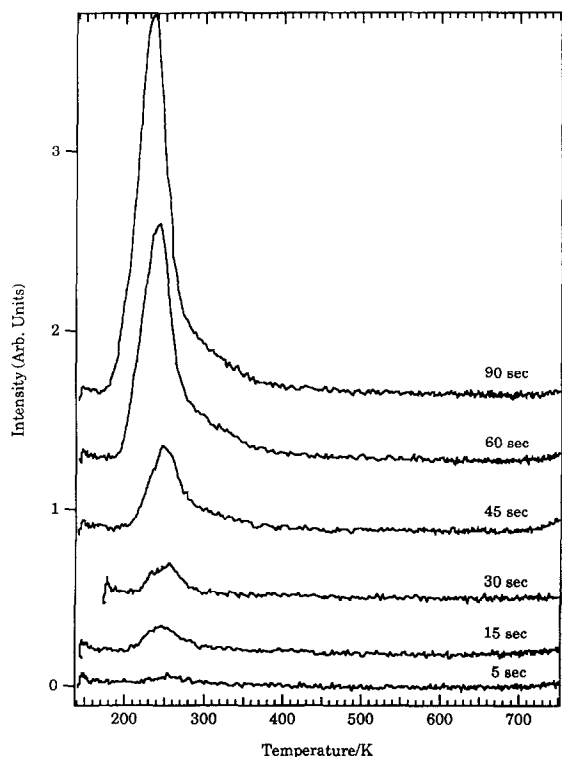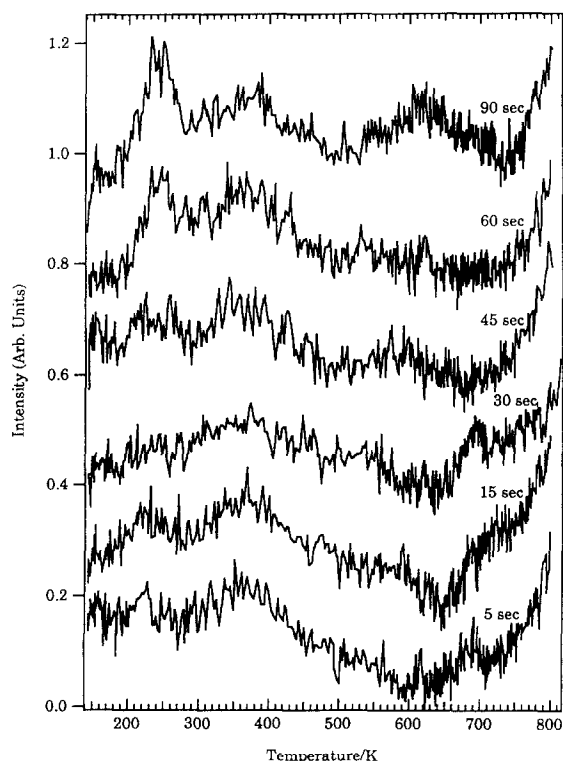

Fig. 6. Hydrogen desorption from hydrazine decomposition on the GaAs(100)-c(8 × 2) surface at various exposures. Heating rate = 6 K/s.

temperature atomic nitrogen recombination peak is observed, nitrogen desorption must occur through an intramolecular process.

3.2. X-ray photoelectron spectroscopy (XPS)

N 1s XPS spectra for a 120 s dose of hydrazine on the clean GaAs(100)-c(8 × 2) surface are shown in Fig. 7. The surface coverage under these conditions should be on the order of one monolayer based on TPD results above. The spectrum from clean GaAs(100) has been subtracted to remove contributions from the GaAs Auger background in this region. A secondary electron background has also been subtracted in the form of a smoothed step function [15]. The pass energy was 22 eV. At 150 K, a peak centered at 400.2 eV with a FWHM = 1.7 eV is observed with a lower binding energy shoulder at 398.5 eV. The 400.2 eV binding energy is character-

Fig. 5. Nitrogen desorption from hydrazine decomposition on the GaAs(100)-c(8 × 2) surface at various exposures. Heating rate = 6 K/s.
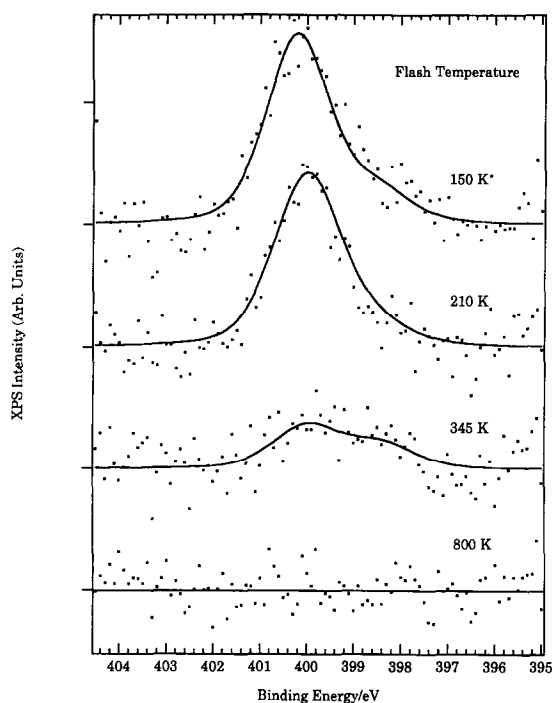
Fig. 7. XPS spectra for a 120 s exposure of hydrazine on the GaAs(100)-c(8 × 2) surface and subsequent anneal to the indicated temperatures. Pass energy = 22 eV. Dots are the actual data points, solid lines are fitted spectra.

istic of monolayer hydrazine. Binding energies for monolayer hydrazine have been reported on Fe(111) [22] and Rh(100) [18] at 400.1 eV and on Pt(111) [17] at 400.2 eV. The narrow FWHM is indicative of hydrazine bonding in a "side on" instead of an "end on" fashion. An "end on" bonding geometry would result in two distinct chemical environments for nitrogen which are observable by XPS as a broad N 1s peak with a FWHM of approximately 3.8 eV [23–25]. The "end on" bonding geometry for N_2H_4 in Mn complexes has been reported [23], as have XPS data for dinitrogen complexes with Re [24] and Rh [25]. "Side on" bonding of N_2H_4 has been reported on the Fe(111) [22] and Pt(111) [17] surfaces with FWHM on the order of 1.8 eV in both cases. The lower binding energy shoulder in the N 1s 150 K spectrum is attributed NH_x ($x = 1, 2$) species. NH_x species have been reported on GaAs(100)-(4 × 6) at 398.5 eV [26] and on Si(100)-(2 × 1) at

398.0 eV [27]. Upon annealing the sample to 210 K, the major peak shifts to 400.0 eV (FWHM = 1.7 eV) with the lower binding energy shoulder remaining at 398.5 eV, indicating the presence of surface hydrazine and NH_x species.

TPD experiments indicate that all molecular hydrazine has desorbed from the surface by 300 K. HREELS results (below), however, indicate that all N–N bonds have not been broken. The XPS data for a hydrazine monolayer annealed to 345 K show a peak with components centered at 399.9 and 398.5 eV. The broad peak has contributions from N_2H_y species at higher binding energy, while at lower binding energy, the NH_x species are the major contributors [22,26,27]. By 800 K, all nitrogen containing species have desorbed from the surface.

Similar XPS experiments were performed when the substrate temperature was held at the various annealing temperatures upon dosing. The results were the same as presented above.

XPS data show that hydrazine binds to the GaAs(100)-c(8 × 2) surface in a "side on" fashion as evidenced by the narrow peak widths. At 345 K, some N–N bonds are still intact, but in the form of N_2H_y ($y = 1, 2, 3$) species. NH_x ($x = 1, 2$) species are also present on the surface at this temperature. By 800 K, all nitrogen containing species have desorbed from the surface.

3.3. High resolution electron energy loss spectroscopy (HREELS)

The vibrational spectrum for a 20 min dose of hydrazine adsorbed on the GaAs(100)-c(8 × 2) surface at 130 K is shown in Fig. 8. The major features and assignments are found in Table 1. The clean GaAs(100) spectrum is dominated by the surface optical phonon at 287 cm^{-1}. Major loss features after 20 min hydrazine exposure are observed in the 900–1800 and 2500–3500 cm^{-1} regions. The weak features to the high frequency side of the intense loss features are a combination of the vibrational loss and the optical phonon overtones. The high frequency region of the 130 K spectrum is dominated by a loss at 3363 cm^{-1} with a shoulder to the low frequency side at approximately 3023 cm^{-1}. The 3363 cm^{-1} loss is associated with symmetric and asymmetric N–H stretching modes of the adsorbed hydrazine
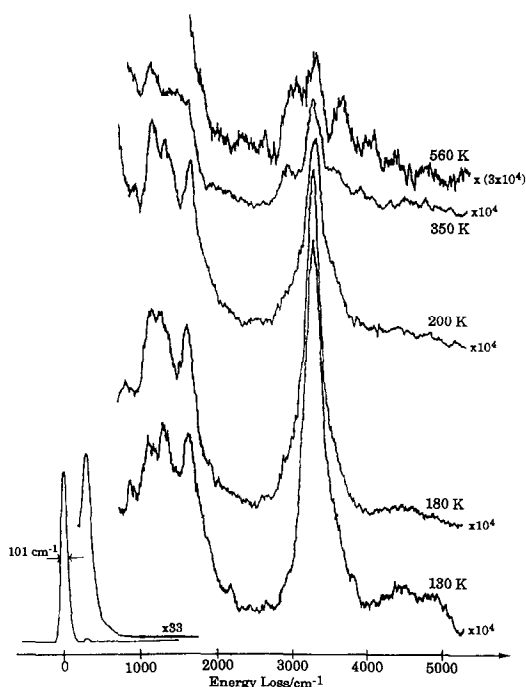
Fig. 8. HREELS spectra for a 20 min exposure of hydrazine on the GaAs(100)-c(8×2) surface and subsequent anneal to the indicated temperatures. The resolution of the spectrometer was 101 cm^{-1}. The features at 2956 and 3049 cm^{-1} in the 350 and 560 K spectra are attributed to C–H and O–H containing impurities [16,34].

molecule. The symmetric and asymmetric modes of adsorbed hydrazine have been observed on Si(111) at 3160 and 3315 cm^{-1}, respectively [28] and on the

Table 1
HREELS vibrational frequencies (in cm^{-1}) and assignments for a 20 min hydrazine exposure on the GaAs(100)-c(8×2) surface

Frequency	Assignment	Temperature observed (K)
909	N_2H_4 rock	130
1182	Combination: N–N stretch NH_3 symmetric deformation	130–180
1295	Ga–NH_2 stretch	180–350
1356	N_2H_4 wag	130–180
1476	NH_2 deformation	350
1619	NH_3 asymmetric deformation	180–200
1671	N_2H_y (y = 1, 2, 3) N–N stretch	130
3023	Hydrogen bonding	130–180
3363	Symmetric and asymmetric N_2H_4 stretch	130–560

Ni(111) surface at 3150 and 3300 cm^{-1} [20]. The stretching modes are visible up to 560 K with a shift in frequency to 3319 cm^{-1} at 350 K, indicating an increase in NH_2 surface concentration. The NH_2 symmetric and asymmetric stretching modes have been observed in the 3232 to 3280 cm^{-1} range [26,29]. The shoulder to the low frequency side of the 3363 cm^{-1} peak at 3023 cm^{-1} is attributed to vibrational modes associated with hydrogen bonding occurring in the adsorbed multilayer [30].

At lower frequency, the loss region is more complex with many overlapping features. Major peaks occur in the 130 K spectrum at 1182, 1356, and 1671 cm^{-1}. The broad feature at 1182 cm^{-1} is most likely a combination of features. The N–N stretching mode on Ni(111) [20] was observed at 1070 cm^{-1} and on Pt(111) [17] at 1077 cm^{-1}. The vibrational loss associated with the NH_3 symmetric deformation mode is also in this region (1220–1190 cm^{-1}) [16,26,29]. Lastly, the overtone of the optical phonon, $4v_p$ should contribute at 1148 cm^{-1}, but this contribution should be quite small relative to the intensity of the vibrational losses. The 1182 cm^{-1} loss feature is therefore assigned to a combination of these three vibrational losses. On annealing as high as 350 K the peak does not shift.

At 130 K a loss feature at 1356 cm^{-1} is observed. This feature is associated with the asymmetric wagging mode of adsorbed hydrazine. The asymmetric wagging mode of hydrazine has been observed on Si(111) [28] and Ni(111) [20] at 1340 cm^{-1} and on Pt(111) [17] at 1392 cm^{-1} [17]. On annealing to 180 K this feature shifts 45 cm^{-1} to 1311 cm^{-1}. The lower frequency peak is most likely due to the combination of the N_2H_4 wag and the Ga–NH_2 stretching mode. The Ga–NH_2 stretch has been observed in the 1279 to 1292 cm^{-1} range [16,31]. After annealing to 200 K, the feature shifts to 1295 cm^{-1}, confirming the appearance of the Ga–NH_2 stretching mode.

The feature at 1671 cm^{-1} in the 130 K spectrum is most likely the N–N stretching mode of adsorbed N_2H_y species where the bond order of the nitrogen atoms is between one and three, i.e., y = 1, 2, 3 [17]. Annealing to 180 and 200 K, the peak shifts to 1649 and 1619 cm^{-1}, respectively. Vibrational loss features in this region are characteristic of the NH_3 asymmetric deformation mode, previously observed at high NH_3 coverages on the GaAs(100)-c(8 × 2)

surface [16] at 1646 cm^{-1} and on the GaAs(100)-(4 × 6) reconstruction [26] at 1600 cm^{-1}. Raising the temperature to 350 K shifts the feature to 1476 cm^{-1}. The deformation mode of adsorbed NH_2 groups at 1483 cm^{-1} is in this same region [16,26]. The 1476 cm^{-1} feature is therefore associated with surface NH_2 group deformation.

The minor feature at 909 cm^{-1} is associated with the NH_2 rocking mode of adsorbed hydrazine, which has been observed at 885 cm^{-1} in solid N_2H_4 [30,32] and at 900 cm^{-1} on the Ni(111) surface [20].

At high coverage, the HREELS data for hydrazine adsorption on the GaAs(100)-c(8 × 2) surface show that N–H bonds are broken at low temperature (130 K) as indicated by the N–N stretching of adsorbed N_2H_y at 1671 cm^{-1}. Increasing the temperature to 180 and 200 K results in further decomposition of the N_2H_y intermediates as evidenced by the appearance of Ga–NH_2 stretching modes at 1295 cm^{-1}. By 350 K, all N–N bonds are broken and the NH_2 deformation mode at 1476 cm^{-1} is evident.

The vibrational spectrum for a 120 s dose of hydrazine on the GaAs(100)-c(8 × 2) surface is in Fig. 9. The overtone of the optical phonon at 575 cm^{-1} ($2\nu_p$) is visible in the 130 K spectrum. Table 2 summarizes the peak positions and assignments for the low coverage HREELS data. The 130 K spectrum has loss features at 1189, 1667, and 3335 cm^{-1}. In analogy to the high coverage data, the 1189 cm^{-1} feature is most likely a combination of the N–N stretching mode of hydrazine and the NH_3 symmetric deformation mode, with a small contribution from the surface optical phonon overtone, $4\nu_p$. This peak has a high frequency shoulder at 1292 cm^{-1} which is in the region of the Ga–NH_2 stretching mode for adsorbed NH_2. Annealing to 200 K shifts the peak maximum to 1167 cm^{-1} while the shoulder remains at 1292 cm^{-1}. The shift of the peak to lower frequency is most likely due to an increased contribution of the phonon overtone upon desorption of the nitrogen containing species from the surface.

At 130 K, the 1667 cm^{-1} feature is, in analogy to the high coverage data, the N–N stretching mode for N_2H_y species. Annealing to 200 K shifts the peak to 1655 cm^{-1}. By 325 K, the peak shifts to 1640 cm^{-1}. The shift to a lower frequency upon increasing the temperature is most likely due to an increase in the
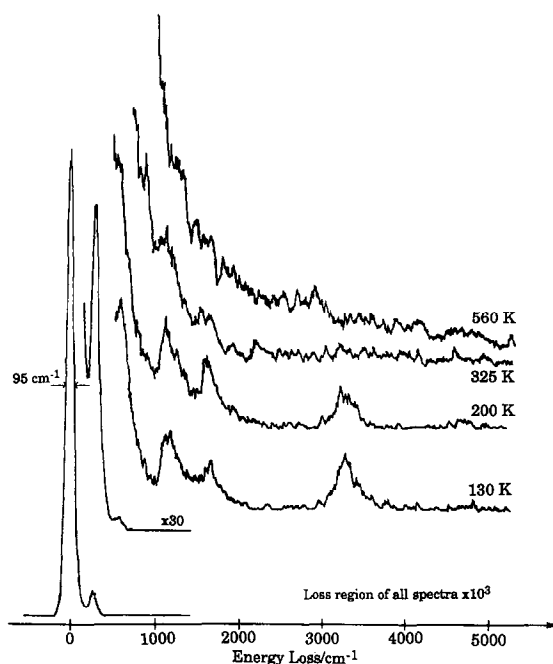

Fig. 9. HREELS spectra for a 120 s exposure of hydrazine on the GaAs(100)-c(8×2) surface and subsequent anneal to the indicated temperatures. The resolution of the spectrometer was 95 cm^{-1}.

concentration of surface NH_3 groups and N–N bond cleavage. The NH_3 asymmetric deformation mode has been observed on the GaAs(100)-c(8 × 2) [16] surface at 1646 cm^{-1} and on the GaAs(100)-c(4 × 6) reconstruction [26] at 1600 cm^{-1}. This phenomenon is analogous to the high coverage data for hydrazine on the GaAs(100)-c(8 × 2) surface.

At 3335 cm^{-1} in the 130 K spectrum are the unresolved loss features associated with the symmet-

Table 2
HREELS vibrational frequencies (in cm^{-1}) and assignments for a 120 s hydrazine exposure on the GaAs(100)-c(8×2) surface

Frequency	Assignment	Temperature observed (K)
1189	Combination: N–N stretch NH_3 symmetric deformation	130–180
1292	Ga–NH_2 stretch	180–350
1667	N_2H_y (y = 1, 2, 3) N–N stretch	130
3335	Symmetric and asymmetric N_2H_4 stretch	130–560

All Products

NH$_x$ N$_2$H$_y$ H N   y=1,2,3,4
x=1,2,3

200 K

NH$_3$
H$_2$

H$_2$N-NH$_2$ 350 -   NH$_x$
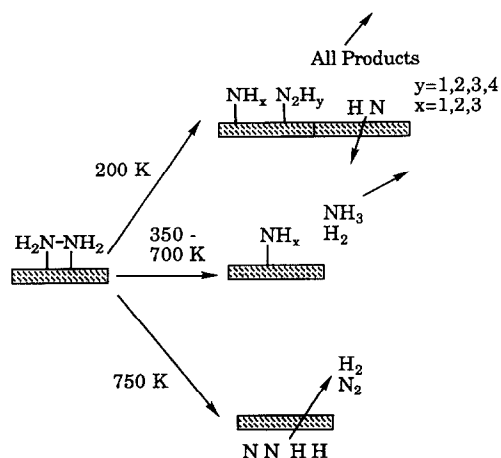700 K

750 K

H$_2$
N$_2$

N N H H

Fig. 10. Schematic of the surface intermediates and gas phase decomposition products for hydrazine adsorption on the GaAs(100)-c(8×2) surface.

ric and asymmetric stretching modes of adsorbed hydrazine. Annealing to 200 K shifts the peak to 3308 cm^{-1} and the peak decreases in intensity. The shift to lower frequency is indicative of the formation of surface NH$_2$ groups (3232 to 3280 cm^{-1}) [26,33]. By 325 K, the intensity of the N–H stretching modes is too weak to be detectable in these experiments [16,29].

The low coverage HREELS data show that both N–N and N–H bonds are broken at low temperature (130 K). At 130 K, the 1292 cm^{-1} loss feature is evidence for surface NH$_2$ group formation, while the 1667 cm^{-1} feature indicates that N$_2$H$_y$ groups ($y = 1, 2, 3$) are also present on the sample surface. With increasing temperature, further decomposition of the N$_2$H$_y$ intermediate occurs as evidenced by the shift in the 1667 cm^{-1} feature to lower frequency (1640 cm^{-1} at 325 K) indicating the presence of surface NH$_3$ groups.

4. Conclusions

The decomposition mechanism for hydrazine on the GaAs(100)-c(8 × 2) surface can be summarized in Fig. 10. Hydrazine adsorbs in a "side on" fashion as evidenced by the narrow peak widths in the XPS spectra. If an "end on" adsorption geometry were favored, distinct chemical environments would be

detectable by XPS. By 200 K, the surface intermediates are N$_2$H$_y$ and NH$_x$ species ($y = 1, 2, 3$; $x = 1, 2$). Recombination of the surface intermediates with adsorbed hydrogen atoms forms hydrazine and ammonia desorption products, respectively. Decomposition of the N$_2$H$_y$ intermediate yields nitrogen gas, as seen in the TPD spectra. On annealing to 350 K, HREELS results indicate that all N–N bonds have been broken, leaving only NH$_x$ species on the surface. The NH$_x$ species recombine with H(ad) to form ammonia as seen by TPD. Above 750 K, subsurface hydrogen and nitrogen migrate back to the surface and desorb.

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