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

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Abstract

The effect of ammonia exposure and substrate temperature on the reaction of ammonia with GaAs(100)-c(8 × 2) has been studied using temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and high resolution electron energy loss spectroscopy (HREELS). TPD data indicate that thermal decomposition of ammonia occurs at moderate temperatures (250 K). Above 250 K, recombinative desorption of ammonia is the dominant reaction mechanism. The appearance of the NH_2 deformation mode at low exposure and temperature indicates thermal decomposition of ammonia on the GaAs(100)-c(8 × 2) surface.

1. Introduction

The ability to grow nitride layers of known structure on semiconductor surfaces is of great importance for device fabrication applications. The replacement of silicon/silicon dioxide based devices with GaAs based technology will provide devices with faster performance times and reduced power requirements. The interaction of ammonia with GaAs surfaces with a view to nitride layer growth is a relatively well studied system. The use of ammonia as a nitrogen source for the chemical vapor deposition (CVD) of gallium nitride has been researched by many groups [1,2]. Typical reactants for this type of growth are trimethyl gallium (TMGa) and ammonia. The growth mechanism is dependent upon NH_3/TMGa molar ratio, substrate temperature, and reactant pressure. A molecular understanding of the interaction of ammonia with the GaAs(100)-c(8 × 2) surface will therefore be helpful in determining the mechanism of CVD growth.

In this work, temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and high resolution electron energy loss spectroscopy (HREELS) are used to determine the mechanism of reaction of ammonia with the GaAs(100)-c(8 × 2) surface.

2. Experimental

All experiments were performed in an ultra-high vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr. The chamber is equipped for temperature programmed desorption (TPD), low energy

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electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and high resolution electron energy loss spectroscopy (HREELS).

The samples were 15 mm × 10 mm slices of *n*-doped GaAs(100) wafers. To provide for resistive heating of the substrate, 3000 Å of Ta was sputter deposited onto the back of each wafer. The wafer slices were mounted onto a liquid nitrogen cooled manipulator capable of 360° rotation using two Ta clips. The temperature was sampled using a thermocouple spot-welded to a third Ta clip which was pressure fitted to the top of the GaAs sample. The surface was cleaned using 500 eV Ar^+ sputtering and high temperature annealing cycles. Sputtering at 733 K for 15 min followed by annealing at 773 K for 15 min and flashing to 875 K provided a clean, ordered c(8 × 2) surface as monitored by AES and LEED. Ammonia was introduced into the chamber through a leak valve. For dosing, the pressure rise in the chamber was kept constant while the dose time was varied. The dosages are reported below as times of exposure.

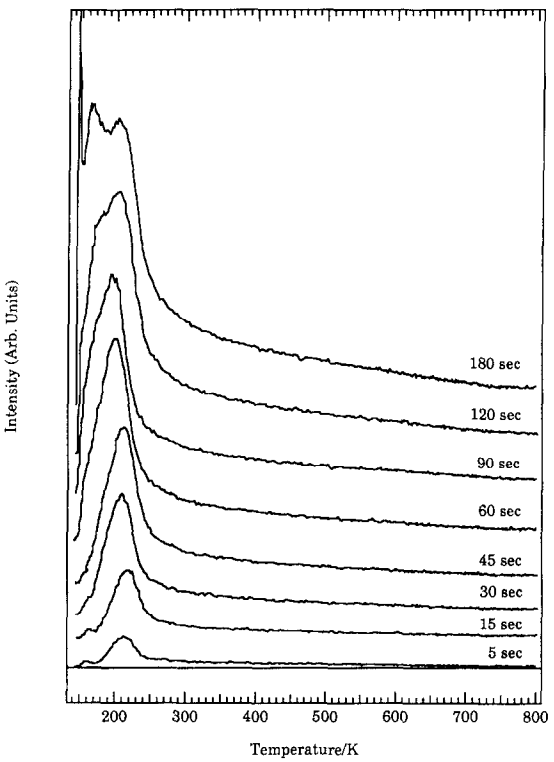

Fig. 1. Ammonia temperature programmed desorption spectra for various exposures on the GaAs(100)-c(8 × 2) surface. The heating rate for all spectra was 6 K/s. The baseline has been included as a guide.

All TPD experiments had a ramp rate of 6 K/s provided by an analog linear voltage ramp generator. The ramp generator provided a linear heating rate over the 180 to 700 K temperature range. Up to ten masses could be monitored during one experiment using a multiplexed mass spectrometer. The sample was placed approximately 1 mm away from the mass spectrometer collimator during the heating cycle to reduce signal from the background and the Ta clips. XPS data were collected using Mg Kα radiation with the sample temperature held at 130 K. A typical data collection time for the N 1s region was 30 min with a pass energy of 44 eV. The nitrogen 1s spectra were normalized to the clean spectrum for the c(8 × 2) surface to eliminate the GaAs Auger background in this energy region. The XPS energy scale was referenced to the Ga 3d levels for bulk GaAs. HREELS spectra were collected at 130 K, 0.6 eV/min scan rate, and a beam energy of 6–7 eV. The resolution of the spectrometer varied from 90 to 113 cm^{-1}.

3. Results and discussion

3.1. Temperature programmed desorption (TPD)

The major gas phase thermal desorption product from ammonia adsorption on the GaAs(100)-c(8 × 2) surface is NH_3 (Fig. 1). Fig. 1 shows ammonia desorption for various dose times, or exposures. At low exposures, one peak centered around 215 K is observed. With increasing exposure, a lower temperature (160 K) state is filled and a high temperature (225–800 K) shoulder becomes increasingly evident. These low temperature states also have been observed for the (4 × 6) [3] and (4 × 1) [4] reconstructions of the GaAs(100) surface. The 160 K peak is assigned to physisorbed ammonia and the 215 K peak to chemisorbed ammonia in agreement with previous data [3–5]. The high temperature shoulder is assigned to the NH_2(ad) + H(ad) recombination. This recombination has been observed previously on the (4 × 1) reconstructed surface [4] which is closely

related in structure to the c(8 × 2) reconstruction, and is in good agreement with data shown below.

3.2. X-ray photoelectron spectroscopy (XPS)

To provide an internal standard for the detection of GaN by XPS, the clean GaAs(100)-c(8 × 2) surface was sputtered in a nitrogen ambient. The result of a thirty minute sputter treatment with a 500 eV beam energy in a nitrogen ambient is shown in Fig. 2 for sputtering temperatures of 145 and 773 K. At high temperature, (Fig. 2, squares) a broad peak from 397–403 eV shows the deposition of only NH_x ($x = 1, 2, 3$) species [6]. At low temperature (Fig. 2, circles), sputtering in a nitrogen ambient results in a 396.5 eV (FWHM = 1.5 eV) binding energy peak with a high energy shoulder to approximately 405 eV. The 396.5 eV binding energy peak is characteristic of GaN formation [3,6], while the high energy shoulder shows formation of NH_x species during low temperature sputtering.

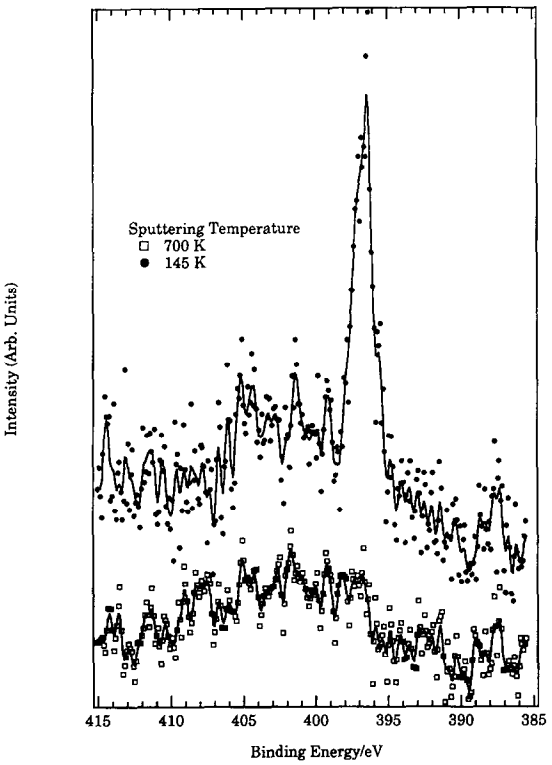

Fig. 2. Nitrogen 1s XPS spectra after 30 min sputter treatment in nitrogen ambient. Substrate temperatures during sputter treatment were 700 (□) and 145 K (●). Pass energy = 44 eV.

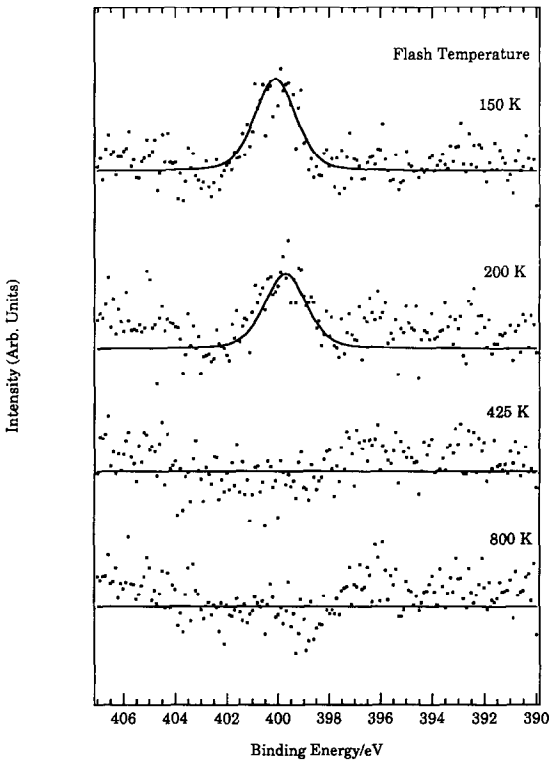

Fig. 3. Nitrogen 1s XPS spectra after a 600 s ammonia dose on the GaAs(100)-c(8 × 2) surface at 150 K and subsequent anneal to the indicated temperatures. Pass energy = 44 eV. Dots are the actual data points, solid lines are fitted spectra.

The XPS N 1s spectrum after ammonia adsorption on the c(8 × 2) surface is shown in Fig. 3. For all nitrogen 1s spectra shown here, the N 1s spectrum from the clean GaAs(100)-c(8 × 2) surface has been subtracted to remove the contributions from the GaAs Auger background. The top spectrum shows the N 1s region after a 600 s dose of ammonia at a sample temperature of 130 K. The surface coverage under these conditions should be on the order of one monolayer, as the NH_3 multilayer desorption temperature is under 100 K [7]. The spectrum, collected at 150 K, shows one peak (FWHM = 1.7 eV) centered at 400.1 eV. Physisorbed ammonia has been observed on the Si(100) surface [8,9] and the GaAs(100)-(4 × 6) reconstruction [3,6] at this binding energy. The peak is therefore assigned to molecular ammonia physisorbed to the GaAs(100)-

c(8 × 2) surface. Annealing to 200 K shows a 20% decrease in intensity corresponding to the first thermal desorption peak. The peak energy also shifts to 399.8 eV which indicates a small change in composition of the adsorbed layer from physisorbed molecular ammonia to chemisorbed molecular ammonia. Further annealing to 425 and 800 K shows the removal of all nitrogen containing species from the surface. The 150 and 200 K spectra demonstrate that the majority of the ammonia adsorbs and desorbs molecularly from the physisorbed and chemisorbed states on the GaAs(100)-c(8 × 2) surface.

3.3. High energy electron energy loss spectroscopy (HREELS)

Vibrational data for large ammonia exposure on the GaAs(100)-c(8 × 2) surface are shown in Fig. 4. The HREELS spectrum of clean GaAs(100) is dominated by a surface optical phonon loss peak at 288 cm^{-1}. The HREELS peak positions and assignments for high ammonia exposure are in Table 1. After a 20 min ammonia dose at 130 K, the bottom spectrum in Fig. 4 was obtained. The 130 K adsorbed ammonia spectrum has major loss features at 1226, 1646, and 3406 cm^{-1}. The weak features at the high energy side of the loss peaks are a combination of the vibrational loss peaks and optical phonon losses. The adsorbate related losses are characteristic of adsorbed ammonia on the GaAs(100) surface [3,4,10]. The loss feature at 1226 cm^{-1} is assigned to the symmetric deformation mode of adsorbed NH_3. Annealing to 185 K shifts the peak to 1264 cm^{-1}, 38 cm^{-1} to higher frequency with a shoulder to lower frequency evident. The shift to higher frequency may be attributed to the formation of NH_2 groups on the surface. The Ga–NH_2 stretching mode has been observed between 1279 and 1292 cm^{-1} [2]. The low frequency shoulder, at approximately 1137 cm^{-1}, is an overtone of the surface optical phonon, $4\upsilon_p$. At 255 K, the loss feature is positioned at 1250 cm^{-1} with a shoulder at 1384 cm^{-1} becoming evident. The shoulder grows into a peak at 1451 cm^{-1} upon annealing to 555 K, indicating the presence of surface NH_2 groups, and consistent with TPD data. The surface NH_2 group has been observed on the GaAs(100)-(4 × 6) surface [3], with the deformation (scissor) mode at 1483 cm^{-1}.

The major feature at 1646 cm^{-1} in the 130 K spectrum is attributed to the degenerate deformation mode of surface NH_3. At 185 K, the feature decreases in intensity and is positioned at 1650 cm^{-1}. By 225 K, the peak shifts 41 cm^{-1} to 1609 cm^{-1},

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

Frequency	Assignment	Temperature observed (K)
618	Ga–N stretch	130–255
985	Ga–NH_3 rock	255
1226	Symmetric NH_3 deformation	130–555
1451	NH_2 deformation	255–555
1646	Asymmetric NH_3 deformation	130–555
2991	Hydrogen bonding	130–185
3406	Symmetric and asymmetric NH_3 stretch	130–255

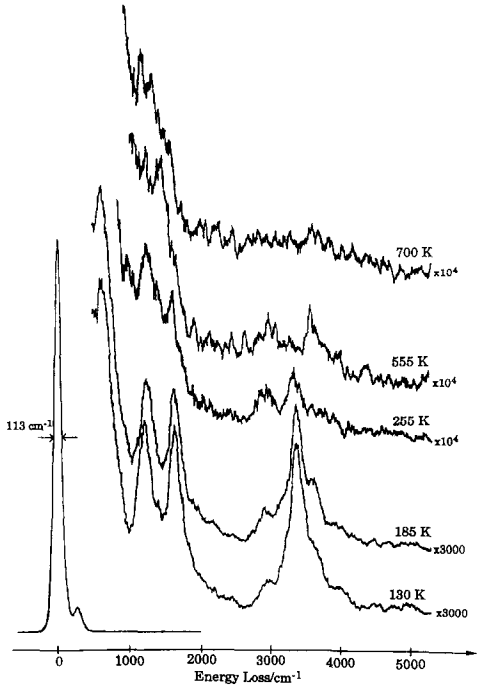

Fig. 4. HREELS spectra after 20 min ammonia dose on the GaAs(100)-c(8 × 2) surface and subsequent anneal to the indicated temperatures. Spectrometer resolution was 113 cm^{-1}. The features at 2956 and 3049 cm^{-1} in the 350 and 560 K spectra are attributed to C–H and O–H containing impurities [12].

still within the range for the NH_3 degenerate deformation mode [3,4].

At 130 K, a high frequency loss feature is observed at 3406 cm^{-1}. This feature is associated with the unresolved vibrational loss for the symmetric and asymmetric stretching modes of adsorbed ammonia [3,4,10]. By 185 K, the feature decreases in intensity, consistent with TPD results, and is positioned at 3411 cm^{-1}. Annealing to 255 K shifts the feature to 3355 cm^{-1}. The shift of 55 cm^{-1} to lower frequency moves the peak closer to the characteristic frequency of N–H stretching modes of surface NH_2 groups observed previously in the 3232 to 3280 cm^{-1} range [3,10]. This indicates that the adsorbed layer is composed of both NH_3 and NH_2 groups at 255 K. Upon annealing to 555 K, the 3355 cm^{-1} feature is essentially gone. Due to the small surface coverage at these temperatures, as indicated by the small intensity of the 1234 cm^{-1} loss feature, the intensity of the higher frequency stretching mode is too small to be observed [3,10].

Minor loss features at 618 and 2991 cm^{-1} are also observed at high coverage on the GaAs(100)-c(8 × 2) surface. The feature at 618 cm^{-1} is most likely the Ga–N stretching mode for adsorbed NH_3. The Ga–N stretching mode for highly hydrogenated gallium nitride was observed by Kouvetakis and Beach using infrared (IR) spectroscopy as a broad band centered around 550 cm^{-1} [11]. The bandwidth of the IR peak narrowed significantly upon removal of hydrogen from the film, but the energy of the peak did not shift. The loss feature at 2991 cm^{-1} which upon annealing to 185 K, sharpens and shifts to 2929 cm^{-1} has been previously observed on GaAs(100)-(4 × 1) [4] and is assigned to vibrational losses associated with ammonia cluster formation on the surface.

For large exposure and moderate temperature (as low as 255 K), the HREELS data show evidence for thermal decomposition of ammonia on the GaAs(100)-c(8 × 2) surface, consistent with TPD and XPS results. By 555 K, the 1451 cm^{-1} loss feature indicates that NH_2 is the dominant surface species. The high frequency stretching modes also shift 55 cm^{-1} to lower frequency at 255 K indicating that the adsorbed layer is composed of both NH_3 and NH_2 groups. All nitrogen containing species have desorbed from the surface above 700 K.

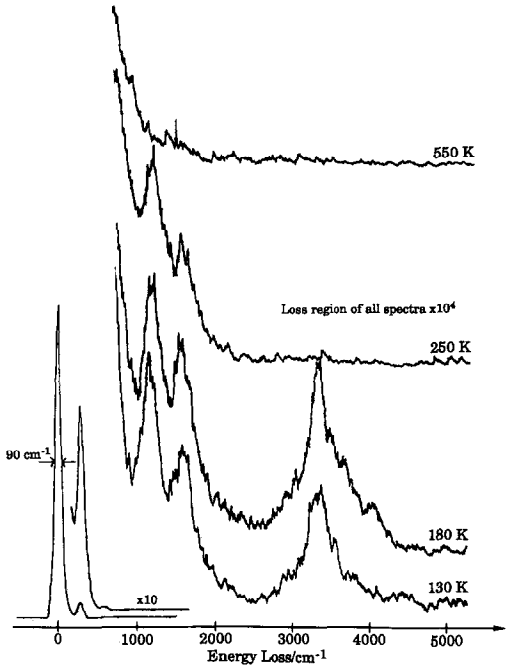

Fig. 5. HREELS spectra after 90 s ammonia dose on the GaAs(100)-c(8×2) surface and subsequent anneal to the indicated temperatures. Spectrometer resolution was 90 cm^{-1}.

An HREELS annealing set for low ammonia coverage is shown in Fig. 5. After a 90 s ammonia dose at 130 K, the bottom spectrum in Fig. 5 was obtained. The HREELS peak positions and assignments for low ammonia coverage are in Table 2. The major loss features are at 1190, 1613, and 3354 cm^{-1}. The 1190 cm^{-1} is attributed to the symmetric deformation mode of surface NH_3. Increasing the temperature to 180 K shifts the peak to 1215 cm^{-1}. The Ga–NH_2 stretching mode has been observed between 1279 and 1292 cm^{-1} [2]. This mode combined

Table 2
HREELS vibrational frequencies (in cm^{-1}) and assignments for a 90 s ammonia exposure on the GaAs(100)-c(8×2) surface

Frequency	Assignment	Temperature observed (K)
1190	Symmetric NH_3 deformation	130–250
1475	NH_2 deformation	180–250
1613	Asymmetric NH_3 deformation	130–180
3354	Symmetric and asymmetric NH_3 stretch	130–250

with the symmetric deformation mode could result in the 1215 cm^{-1} features. Annealing to 250 K shifts the features to 1278 cm^{-1}, confirming the presence of surface NH_2 groups. The 1278 cm^{-1} feature is assigned to the Ga–NH_2 stretching mode.

At 130 K, the 1613 cm^{-1} feature, in analogy with the 20 min dose data is assigned to the degenerate deformation mode of adsorbed ammonia. A shoulder to the low frequency side of the 1613 cm^{-1} peak is also observed at 1475 cm^{-1}. The shoulder is in the region where the NH_2 deformation mode is observed [3], and is therefore indicative of surface NH_2 groups at low coverage and temperature. Upon annealing to 180 K, the feature at 1613 cm^{-1} shifts to 1581 cm^{-1}. The surface NH_2 deformation (scissor) mode has been observed at 1483 cm^{-1} [3]. The shift to lower frequency is a result of the increase in surface NH_2 formation, i.e., N–H bond cleavage. The feature is assigned to a combination of the NH_2 deformation (1483 cm^{-1}) [3] and NH_3 degenerate deformation (1600 cm^{-1}) [3,10] modes.

The broad high frequency loss feature in the 130 K spectrum (3354 cm^{-1}) is attributed to the unresolved symmetric and asymmetric stretching modes of surface NH_3 and NH_2 in analogy with the high coverage data. Upon annealing to 200 K, the peak is positioned at 3395 cm^{-1}. By 325 K, the intensity of the loss feature is too weak to be observed, in analogy with the high coverage HREELS data above.

A 600 cm^{-1} feature (not shown) is also observable at 325 K, consistent with the high coverage HREELS data above, and is therefore assigned to the Ga–NH_3 stretching mode. Annealing to 560 K results in the essentially clean spectrum shown at the top of Fig. 5. Consistent with TPD and XPS results, virtually all surface species have desorbed from the surface by this temperature.

HREELS data for low exposures of ammonia show small amounts of decomposition even at temperatures as low as 130 K. Increasing the temperature results in more decomposition as evidenced by the shifting in frequency of the loss features. By 325 K, the 1278 cm^{-1} Ga–NH_2 stretching mode confirms the presence of surface NH_2 groups. Within the detection limits of the experiment, essentially all nitrogen containing species have desorbed from the surface by 560 K.

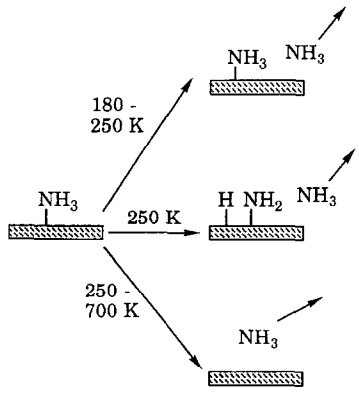

Fig. 6. Schematic of the surface intermediates and gas phase decomposition products for ammonia adsorption on the GaAs(100)-c(8×2) surface.

4. Conclusions

A detailed study of the effect of ammonia exposure and substrate temperature on the decomposition of ammonia on the GaAs(100)-c(8 × 2) surface has been conducted. The TPD, XPS, and HREELS results all show some degree of decomposition of ammonia on the surface at moderate (130–250 K) temperatures. TPD data show that at temperatures above 250 K, NH_2 + H recombination is the dominant desorption channel for ammonia at all exposures. For large exposures, the HREELS data show evidence for adsorbed NH_2 at temperatures as low as 185 K. The shift in the 1264 cm^{-1} peak 38 cm^{-1} to higher frequency is also indicative of the presence of adsorbed NH_2. At low dosage and low temperature, the 1475 cm^{-1} deformation mode of surface NH_2 is apparent, indicating decomposition of ammonia even at these low temperatures.

The decomposition mechanism of ammonia on the GaAs(100)-c(8 × 2) surface can be pictured as shown in Fig. 6.

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