

The adsorption and thermal decomposition of PH_3 and NH_3 on GaAs(100)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 S167

(<http://iopscience.iop.org/0953-8984/3/S/027>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 11:24

Please note that [terms and conditions apply](#).

The adsorption and thermal decomposition of PH_3 and NH_3 on GaAs(100)

N K Singh, A J Murrell, D Harrison and J S Foord

Physical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3Q, UK

Received 25 April 1991

Abstract. The adsorption and thermal decomposition of PH_3 and NH_3 on the Ga-rich GaAs(100)-(4 × 1) has been studied using temperature programmed desorption, isotope exchange reactions and high resolution electron energy loss spectroscopy (HREELS). At 120 K PH_3 adsorbs molecularly while HREELS and isotope exchange reactions with deuterium suggest that PH_2 is the major species present at 300 K. Molecular adsorption is also observed for NH_3 at 150 K when both the physisorbed and chemisorbed states are formed. HREELS and isotope exchange reactions show that dissociation of the molecular state to form NH_2 occurs when the adsorbed phase is heated.

1. Introduction

The reactions of Group V hydrides with semiconductor surfaces are of considerable importance not only because of the interesting surface chemistry they exhibit (Taylor *et al* 1990, Dresser *et al* 1989, Tanaka *et al* 1987) but also because they are widely used in the growth of III-V semiconductors by MOVPE, CBE and GSMBE. The reaction characteristics, however, are not well understood. For example, although it is well known that the hydrides require pre-cracking to form As_2 and P_2 dimers before any growth is observed in CBE and GSMBE it is not known why this should be so. In this paper we report results of our investigations on the adsorption and decomposition behaviour of two group V hydrides, PH_3 and NH_3 , on GaAs(100).

2. Experimental details

The experiments described in this paper were performed in a stainless steel UHV system with a base pressure of $< 10^{-10}$ mbar, equipped with facilities to perform thermal desorption spectrometry, LEED and Auger electron spectroscopy, high resolution electron energy loss spectroscopy, which has been described previously (Murrell *et al* 1990). An n-type semi-insulating GaAs(100) (chromium doped, 10^{17} cm^{-3}) was used in this study and this was cleaned in vacuum by cycles of sputtering with a 500 eV argon ion beam and annealing to 740 K. This procedure resulted in a clean GaAs(100)-(4 × 1) surface as determined by AES and LEED.

3. Results

3.1. PH_3 adsorption and thermal decomposition

Figure 1 shows temperature programmed desorption (TPD) spectra tuned to PH_3 following a wide range of exposures of PH_3 on the GaAs(100)-(4 × 1) surface at 140 K. Two desorption peaks are distinguishable, both broad and arising together at very low exposures. However, at higher exposures the narrow lower temperature peak centred at 260 K increases in intensity faster than the broader peak at 300–500 K and broadens on the low temperature side, the peak maximum shifting to 200 K. No saturation coverage is observed and this is indicative of multilayer formation at this point. Application of the Redhead equation (Redhead 1962) to the lower temperature peak, using a pre-exponential factor of 10^{13} s^{-1} and a heating rate of 11 K s^{-1} , gives a desorption activation energy of 49 kJ mol^{-1} for the multilayer state.

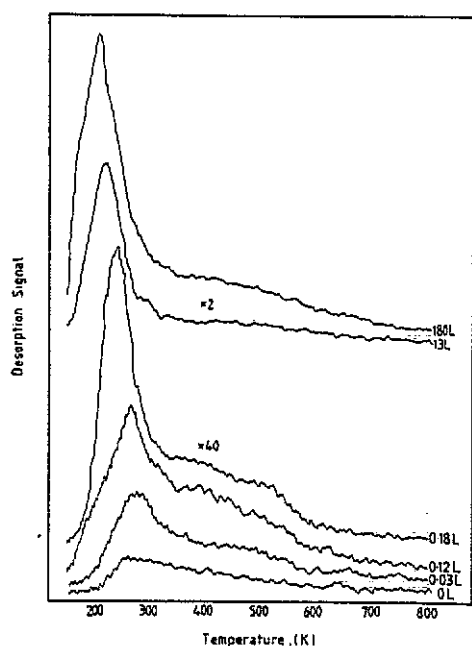


Figure 1. PH_3 TPD spectra following exposures as indicated on GaAs(100) at 140 K.

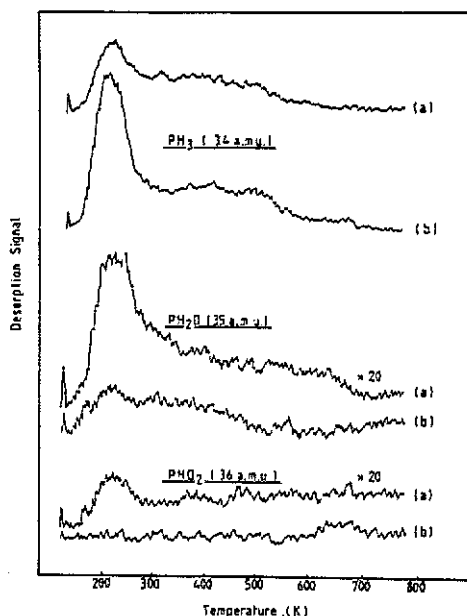


Figure 2. TPD tuned to PH_3 , PH_2D and PHD_2 following exposures at 140 K of (a) 30L D_2 followed by 0.2L PH_3 , (b) 0.2L PH_3 .

Comparable TPD spectra taken for adsorption at 300 K showed the high temperature peak more distinctly, with a peak maximum at 425 K which did not shift with surface coverage. As for adsorption at 140 K this peak was again observed to saturate at high exposures. Using the Redhead equation the binding energy of this state is calculated to be 106 kJ mol^{-1} . The initial sticking probability at 300 K derived from the desorption peak areas is found to be a factor of 20 times smaller than that at 140 K.

HREELS was used to examine further the surface states giving rise to the above observed desorption features. Two loss features at 122 and 288 meV were observed

for the PH_3 covered surface and these can be assigned from gas phase infrared data for PH_3 (Conaghie and Nielsen, 1953) as arising from the symmetric deformation (122 meV) and symmetric stretch (288 meV) modes of PH_3 . The loss values observed in this study are in excellent agreement with those in the published literature. On annealing the surface to 270 K the intensities of the loss peak drop and the 122 meV loss peak was found to shift to 131 meV while the 288 meV peak remains at approximately the same value. Comparison of the IR data for complexes CH_3PH_2 , $(\text{CH}_3)_2\text{PH}$ and SiH_3PH_2 (Linton and Nixon, 1959) and the HREELS data recorded for the annealed surface indicates PH_2 as the most likely surface species at 270 K.

Isotope exchange reactions with deuterium and PH_3 were carried out to confirm the species produced when PH_3 is adsorbed at 140 K and 300 K. Figure 2 shows TPD spectra tuned to $\text{PH}_x\text{D}_{3-x}$ ($x = 1-3$) after a 30 L D_2 (cracked by the mass spectrometer filament) exposure followed by 0.2 L of PH_3 . Also shown in figure 2 are TPD spectra tuned to PH_3 after 0.2 L dose of PH_3 on clean GaAs. Pre-adsorption of deuterium results in a decrease in the PH_3 intensity, as expected, and an increase in the PH_2D TPD intensity. The profile for the PH_2D TPD is similar to that for the original PH_3 TPD but with a less intense low temperature peak relative to the high temperature peak. Both peaks therefore show isotopic scrambling, the higher temperature peak to a greater extent.

3.2. NH_3 adsorption and thermal desorption

Figure 3 shows TPD spectra tuned to NH_3 following adsorption at 150 K. As for PH_3 two desorption peaks are observed, a higher temperature broad peak and a narrow low temperature peak. However, the uptake characteristics of the two systems differ. At low NH_3 exposures only the higher temperature state is observed centred at about 300 K, giving a desorption activation energy of 74 kJ mol^{-1} using the Redhead equation. The narrow peak is only observed at higher exposures once the broader peak has reached a saturation intensity, and is initially centred at 170 K, giving an approximate binding energy of 41 kJ mol^{-1} . Both peaks also show a significant dependence on coverage. Thus the high temperature peak broadens prominently to lower temperatures with increasing coverage, while the sharp peak exhibits fractional order desorption kinetics with a peak position that shifts up with coverage. A TPD spectrum tuned to H_2 showed a small but resolvable peak at 570 K which was only observed for high NH_3 coverages.

HREELS spectra, figure 4, taken following 50 L exposure at 130 K and then following sequential anneal-cool cycles to increasing temperatures, were used to identify surface species formed on adsorption and after thermal decomposition. The NH_3 covered surface at 130 K showed three loss peaks of similar intensity centred at 150, 204 and 417 meV. The loss peaks have been assigned, using vibrational data reported previously for gas phase NH_3 (Herzberg, 1945), adsorbed NH_2 and NH species (Tanaka *et al* 1987, Bassignana *et al* 1986) and $(\text{SiEt}_3)_2\text{NH}$ and $(\text{SiEt}_3)\text{NH}_2$ complexes (Marchand *et al* 1964), to NH_3 modes. The peaks correspond to symmetric deformation (150 meV), the asymmetric deformation (240 meV) and the symmetric and asymmetric stretches unresolved together at 417 meV. As for PH_3 , the loss peaks are in good agreement with the literature values. On annealing the sample to 285 K and then to 400 K the intensities of the 204 and 417 meV peaks decrease. In addition, a progressive shift in the 150 meV loss peak is observed, the peak broadening to lower energy after annealing to 285 K and sharpening at 146 meV by 400 K. The 204 meV peak is also observed to broaden in this data as the annealing temperature is increased to produce

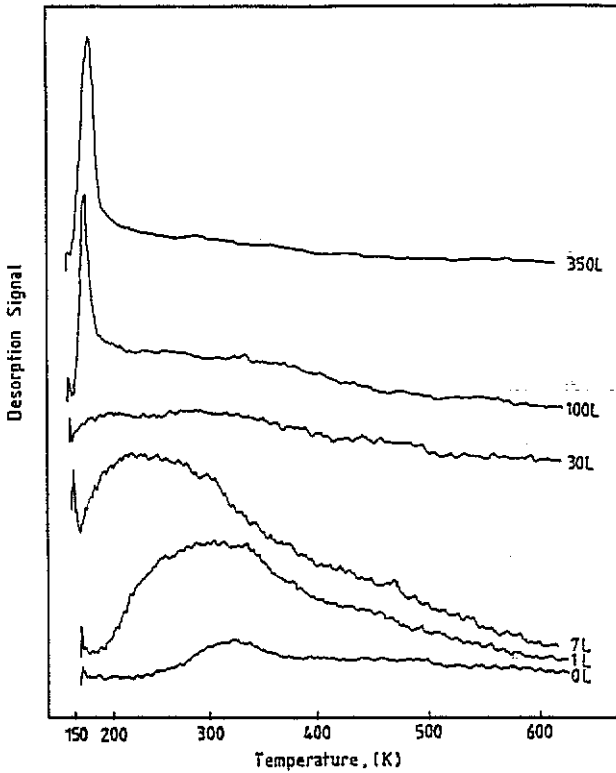


Figure 3. NH_3 TPD spectra following indicated exposures on GaAs(100) at 140K.

a fourth resolvable peak at 189 meV. This energy is in good agreement with the values reported for the NH_2 symmetric deformation or the scissoring mode and was also observed for NH_3 on Ni(110) (Bassignana *et al* 1986). Finally, heating to 705 K reduces all these modes virtually to zero indicating the desorption of all adsorbed species.

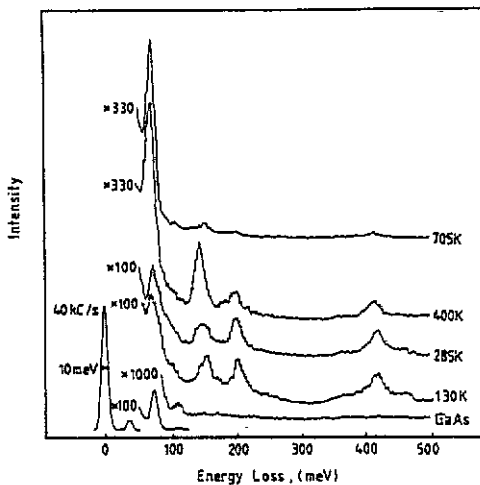
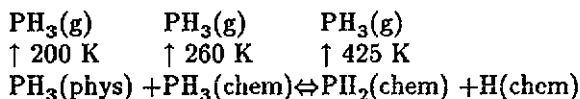


Figure 4. HREELS for a 50L NH_3 exposure on GaAs(100) and after annealing to the temperatures indicated.

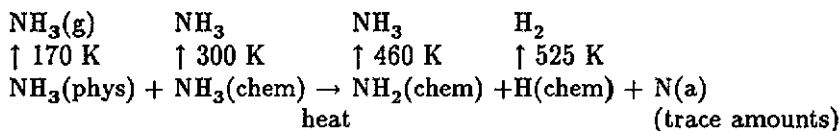
Deuterium co-adsorption experiments were carried out to identify the adsorbed species on the surface. TPD spectra were taken tuned to NH_3 , NH_2D and NHD_2 for a 60 L D_2 exposure followed by 70 L of NH_3 at 150 K substrate temperature. The NH_3 TPD showed the expected profile with two desorption features observed previously, figure 3. Neither of the two desorption peaks are observed in the NH_2D or NHD_2 spectra. A new feature was, however, observed in the NH_2D spectrum centred at 460 K. TPD, tuned to HD, taken after co-adsorption of D_2 and NH_3 showed a peak at 530 K while no peak was observed when D_2 or NH_3 were adsorbed on their own. The peak at 530 K is, therefore, assigned to recombinative desorption of surface D and H atoms, the latter being produced by the thermal cracking of adsorbed NH_3 . HREELS spectra taken following D_2 - NH_3 co-adsorption at 165 K did not give any evidence for isotopic scrambling at this temperature, or when the sample was annealed to higher temperatures. The broadening of the 204 meV loss peak, however, was again observed to occur. These results suggest that although the NH_2 species is produced on the sample when it is annealed, the isotope scrambling observed in the NH_2D TPD spectrum must occur during the temperature ramp.

4. Discussion

The adsorption of PH_3 at 140 K yields two prominent PH_3 desorption peaks which both populate at low coverages. The concurrent uptakes of these peaks indicate that they originate from the same adsorption state, while the HREELS data shows the stable phase to be PH_3 . If the lower temperature desorption peak arises from direct desorption of this species, the higher temperature peak must arise from the recombination of more thermally stable intermediates on the surface. The observation of PH_3 as the desorption product and the HREELS data at 270 K are both consistent with these intermediates being $\text{PH}_2(\text{a})$ and $\text{H}(\text{a})$ and these species must be present following adsorption both at 140 and 300 K. At higher coverages the lower temperature desorption peak is observed to increase in intensity very rapidly and broadens to lower temperatures to produce a third bound state. The uptake behaviour into this third state is characteristic of a multilayer state and was found to desorb all as PH_3 below 250 K. We can summarise the adsorption and desorption behaviour of PH_3 as:



Adsorption of NH_3 at 150 K also yields two clearly resolved NH_3 desorption peaks. However, HREELS indicates that both arise from adsorbed surface NH_3 and the uptake characteristics and desorption profiles lead to their assignments as chemisorbed and physisorbed NH_3 states. This behaviour is similar to that for NH_3 adsorption on Ni(100) (Klauber *et al* 1985) but differs from dissociative absorption observed in Si(111) (Tanaka *et al* 1987) in which NH_2 is the submonolayer state formed at 300 K. HREELS and co-adsorption experiments reveal the presence of NH_2 as a third thermally induced surface state, accounting for the broadness of the NH_3 high temperature TPD peak at all coverages. A reaction scheme, similar to that for PH_3 is:



5. Conclusion

PH_3 and NH_3 both show three adsorption states on the GaAs(100) surface, these being XH_2 ($X = \text{N}, \text{P}$) and submonolayer and multilayer XH_3 states. While the PH_2 species is produced on the surface during adsorption either at 120 K or 300 K, the NH_2 species is formed on the surface by thermal cracking. However, in neither system is thermal cracking observed beyond the XH_2 state. This explains why precracking of the group V hydrides is essential for any semiconductor growth to occur.

References

- [1] Bassignana I C, Wagemann K, Küppers J and Ertl G 1986 *Surf. Sci.* **175** 22
- [2] Conaghie V M and Nielson H H 1953 *J. Chem. Phys.* **21** 1836
- [3] Dresser M J, Taylor P A, Wallace R M, Choyke W J and Yates J T Jr 1989 *Surf. Sci.* **218** 75
- [4] Herzberg G 1945 *Vibrational Infrared and Raman Spectra of Polyatomic Molecules* (New York: Van Nostrand)
- [5] Klauber C, Alvey M D and Yates J T Jr 1985 *Surf. Sci.* **154** 139
- [6] Linton H R and Nixon E R 1959 *Spectrochim. Acta* **15** 147
- [7] Marchand A, Forel M T, Metros F and Valade J 1964 *J. Chim. Phys.* **61** 343
- [8] Murrell A J, Price R J, Jackman R B and Foord J S 1990 *Surf. Sci.* **227** 197
- [9] Redhead P A 1962 *Vacuum* **12** 203
- [10] Tanaka S, Onchi M and Nishijima M 1987 *Surf. Sci.* **191** L756
- [11] Taylor P A, Wallace R M, Choyke W J and Yates J T Jr 1990 *Surf. Sci.* **238** 1