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The nature of the NH_3 adsorption process on Si(100) at 120 K was studied by isotopic mixing with adsorbed atomic deuterium and thermal desorption spectroscopy. NH_3 was found to dissociatively adsorb onto Si(100) dimers sites at 120 K as $NH_2(a)$ and H(a). The $NH_2(a)$ species persist up to about 700 K where two reaction channels become available. The major reaction channel leads to the decomposition of $NH_2(a)$ to N(a) and H(a). The minor channel is a recombination reaction that leads to the desorption of ammonia. This recombination reaction exhibits a deuterium kinetic isotope effect.

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The Dissociative Adsorption of Ammonia on Si(100)

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Abstract

The nature of the NH_3 adsorption process on Si(100) at 120 K was studied by isotopic mixing with adsorbed atomic deuterium and thermal desorption spectroscopy. NH_3 was found to dissociatively adsorb onto Si(100) dimers sites at 120 K as $NH_2(a)$ and $H(a)$. The $NH_2(a)$ species persist up to about 700 K where two reaction channels become available. The major reaction channel leads to the decomposition of $NH_2(a)$ to $N(a)$ and $H(a)$. The minor channel is a recombination reaction that leads to the desorption of ammonia. This recombination reaction exhibits a deuterium kinetic isotope effect.

A. Introduction

The reaction of ammonia with silicon surfaces to produce silicon nitride thin films by either thermal processes [1] or thermal processes combined with electron stimulated desorption [2] has prompted a number of studies of the adsorption of ammonia on silicon. A wide variety of surface measurement techniques such as STM [2,3], XPS [1,2,4], UPS [2,4,5], HREELS [1], ISS [1], ESDIAD [6,7], AES [8], TPD [1,7], and laser vaporization/FTMS [9] have been employed. Even with the large experimental effort applied to this system, the nature of the NH_3-derived adsorbed species has not been definitely determined. For the Si(100) surface there have been reports of both molecular adsorption [5] and dissociative adsorption at ~ 100 K where processes producing NH_2(a) [9], NH(a) [2] or N(a) [1,4] have been postulated. In the work reported here we demonstrate through isotopic mixing studies with deuterium, that ammonia adsorbs dissociatively on the Si(100) surface, producing NH_2(a) and H(a) at 120 K. Elsewhere we have shown that the NH_2(a) species persist up to about 700 K, where they mainly decompose to produce N(a) and H(a), along with a minor recombination reaction channel to produce NH_3(g) [7].

B. Experimental

A UHV system with a base pressure of 4×10^{-11} Torr was used in these studies, and has been described in detail elsewhere [7]. The desorption studies were performed on a p-type, 10 Ω cm Si(100) crystal cleaned in vacuum by sputtering with a 2keV Ar^+ ion beam and annealing to 1100 K. This procedure resulted in a clean Si(100)-(2x1) surface as determined by AES and LEED [7].

-3-

In this experiment, different coverages of atomic deuterium were adsorbed onto the silicon surface followed by adsorption of ammonia at 120 K. The atomic deuterium was produced by backfilling the UHV chamber with $\sim 1 \times 10^{-8}$ Torr of D_2 and placing the Si crystal in front of a 1 cm diameter W-spiral heated to 1800 K, as shown in Fig. 1. The maximum crystal temperature during deuterium exposure was 315 K. The adsorption of deuterium was followed by the adsorption of NH_3, which was accomplished by rotating the Si(100) crystal into a collimated beam of NH_3 from a calibrated microcapillary array doser [10], shown in Fig. 1, delivering a known flux of ammonia to the crystal [10,11]. Both the adsorption and desorption processes for ammonia were monitored by a digitally multiplexed quadrupole mass spectrometer (QMS) in the geometry shown in Fig. 1.

The relationship between the coverage of D(a) and exposure was determined from temperature programmed desorption calibration experiments, where a heating rate $dT/dt=\beta=1.6K/s$ was employed. The desorption of D_2 from a saturated coverage of D(a) on Si(100) exhibits two desorption features, the monohydride at ~ 780 K and the dihydride at ~ 675 K [12,13]. The monohydride feature is seen for all atomic deuterium exposures. The dihydride desorption feature is observed only above the monolayer coverage [14,15] (monolayer D(a) coverage is achieved at a W-spiral exposure of $D_2 = 6$ Langmuirs, L). From the sequential development of these two features, the D(a) coverage could be determined from the exposure as shown in Fig. 2.

C. Adsorption

In Fig. 3 the adsorption kinetics of NH_3 on the D· pre-exposed Si(100) surface are shown. Before rotating the Si crystal into the NH_3 beam, all surfaces inside the doser assembly were allowed to saturate during the initial period of NH_3 admission to the system (~ 500 seconds). The lower curve in Fig. 3 shows adsorption kinetic experiments for NH_3 on clean Si(100). The adsorption of NH_3 on clean Si(100) is characterized by the drop in the NH_3 signal (at t = 595 s in Fig. 3) upon rotating the crystal into the beam of NH_3 from the doser. The initial drop is followed by a region of constant NH_3 pressure (t = 625-660 s) which indicates that the crystal is adsorbing NH_3 with a constant sticking coefficient, S = 1 to within the accuracy of our measurement methods. The region of S = 1 terminates at a coverage of ~ 3.4×10^{14} ±1.0 NH_3/cm^2 or about one ammonia molecule per Si-Si dimer [7]. (Note: The error shown here involves a propagation of error analysis for all possible errors; the precision of our measurements is considerably better.) After the region corresponding to S = 1, the rate of adsorption decreases and the NH_3 reflected flux from the crystal increases [7].

Pre-adsorbing atomic deuterium caps Si-dangling bond NH_3 adsorption sites and thereby shortens the region of the S = 1 process, as shown by the middle curves in Fig. 3. Pre-adsorbed D(a) also diminishes the slow adsorption process beyond the S = 1 region, as seen by the changing slopes in the data obtained beyond the S = 1 region in Fig. 3. The region of unity sticking coefficient decreases to zero in the D(a) coverge region between 0.99 D/Si and 1.16 D/Si, after which the NH_3 adsorption

is completely quenched. Once this pre-adsorption limit (~ 1 D/Si) has been attained, no further NH_3 adsorption is possible, as seen in the upper two curves in Fig. 3. These results further confirm that the adsorption site of NH_3 is the Si-Si dimer, and that 1 D/Si effectively stops adsorption.
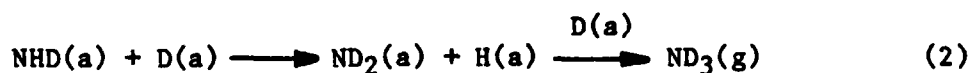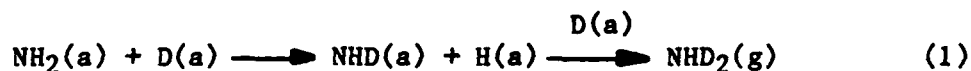
D. Desorption

Upon heating a clean Si(100) crystal exposed to NH_3, two desorbing species are observed, NH_3 and H_2 [7]. For coverages of NH_3 greater than $\sim 3.4 \times 10^{14}$ NH_3/cm^2, two NH_3 desorption features are observed [7], one at 650 K and another below 350 K. As will be shown below, the NH_3 desorption process at 650 K is due to the recombination of $NH_2(a)$ and $H(a)$. This is a minor reaction channel compared to decomposition of $NH_2(a)$ to produce $N(a)$ and $H(a)$ [7]. The lower temperature NH_3 desorption process is due to the release of NH_3 from an adsorbed overlayer and from multilayer NH_3 molecules, and this NH_3 does not exchange with $D(a)$.

The processes leading to recombinative desorption of NH_3 were determined by a study of the isotopic exchange products in the 650 K recombinative process. For $D(a)$ coverages less than 1 D/Si, it was possible to co-adsorb NH_3. A subsequent thermal desorption study produced the following desorption species: H_2, HD, D_2, NH_3, NH_2D, NHD_2, and ND_3. The desorption of these species from NH_3 adsorbed on a D-pre-exposed surface with a coverage of 0.81 D/Si is shown in Fig. 4.

Upon thermal desorption, no isotopic mixing occurs from the low-temperature molecularly-adsorbed NH_3 species (Fig. 4A). Isotopic exchange is observed for ammonia desorbing above 650 K. As shown in Fig. 4B, isotopically mixed hydrogen species are also observed. The

$NH_2(a)$ stoichiometry is confirmed from the ratios of the desorbing species NH_xD_{3-x}. In Fig. 5 the relative yields of NH_xD_{3-x} species are shown over a range of $D(a)$ coverage. Since NH_2D predominates as a desorption product compared to NHD_2 and ND_3 species over the entire range of $D(a)$ coverage, it follows that $NH_2(a)$ is the majority surface species resulting from the dissociative adsorption of NH_3 on $Si(100)$ or from the dissociative adsorption of NH_3 on $Si(100)$ precovered with a partial monolayer of $H(a)$. NHD_2 and ND_3 desorption species arise from consecutive isotope exchange processes through the surface reactions:

$$NH_2(a) + D(a) \longrightarrow NHD(a) + H(a) \xrightarrow{D(a)} NHD_2(g) \qquad (1)$$

$$NHD(a) + D(a) \longrightarrow ND_2(a) + H(a) \xrightarrow{D(a)} ND_3(g) \qquad (2)$$

These results clearly indicate that $NH(a)$, if present at all, is a minority species upon dissociative NH_3 adsorption on $Si(100)$.

The identification of the $NH_2(a)$ surface species is based upon the distribution of isotopic NH_xD_{3-x} recombination species, which occurs in a minor reaction channel. If the major reaction channel, converting NH_3 to $N(a)$ and $H(a)$, also proceeds through $NH_2(a)$, then we can be confident that $NH_2(a)$ is the dominant surface species produced from NH_3.

A close examination of the desorbing ammonia species shows a shift in desorption temperature maxima with an increasing incorporation of deuterium. This phenomenon indicates that a deuterium kinetic isotope effect is present in the elementary step controlling NH_3 desorption. Therefore, the rate determining step for ammonia desorption is related to the zero point vibrational energy of a hydrogen-containing surface species in the elementary step of NH_3 formation from $NH_2(a) + H(a)$. It

is likely that this deuterium kinetic isotope effect is due to the loss of a Si-H vibrational mode in the formation of the transition complex for the recombination of $NH_2(a) + H(a)$ to yield the desorption product NH_3. Speaking approximately, an Si-H vibration is converted to the reaction coordinate for the NH_3 production step. Similar effects are observed for $H(a) + H(a) \rightarrow H_2(g)$ on Si(100) [16], as well in the hydrogen recombination process observed here.

E. Conclusions

From adsorption and thermal desorption of NH_3 on deuterium covered Si(100), the stoichiometry of the surface species derived from NH_3 adsorption on Si(100) was determined. It was found that NH_3 dissociatively adsorbs at the Si-Si dimers producing $NH_2(a)$ and $H(a)$ surface species. Upon heating, the $Si-NH_2$ and Si-H surface species undergo recombination to produce $NH_3(g)$ in a minor reaction channel compared to $NH_2(a)$ thermal decomposition [7].
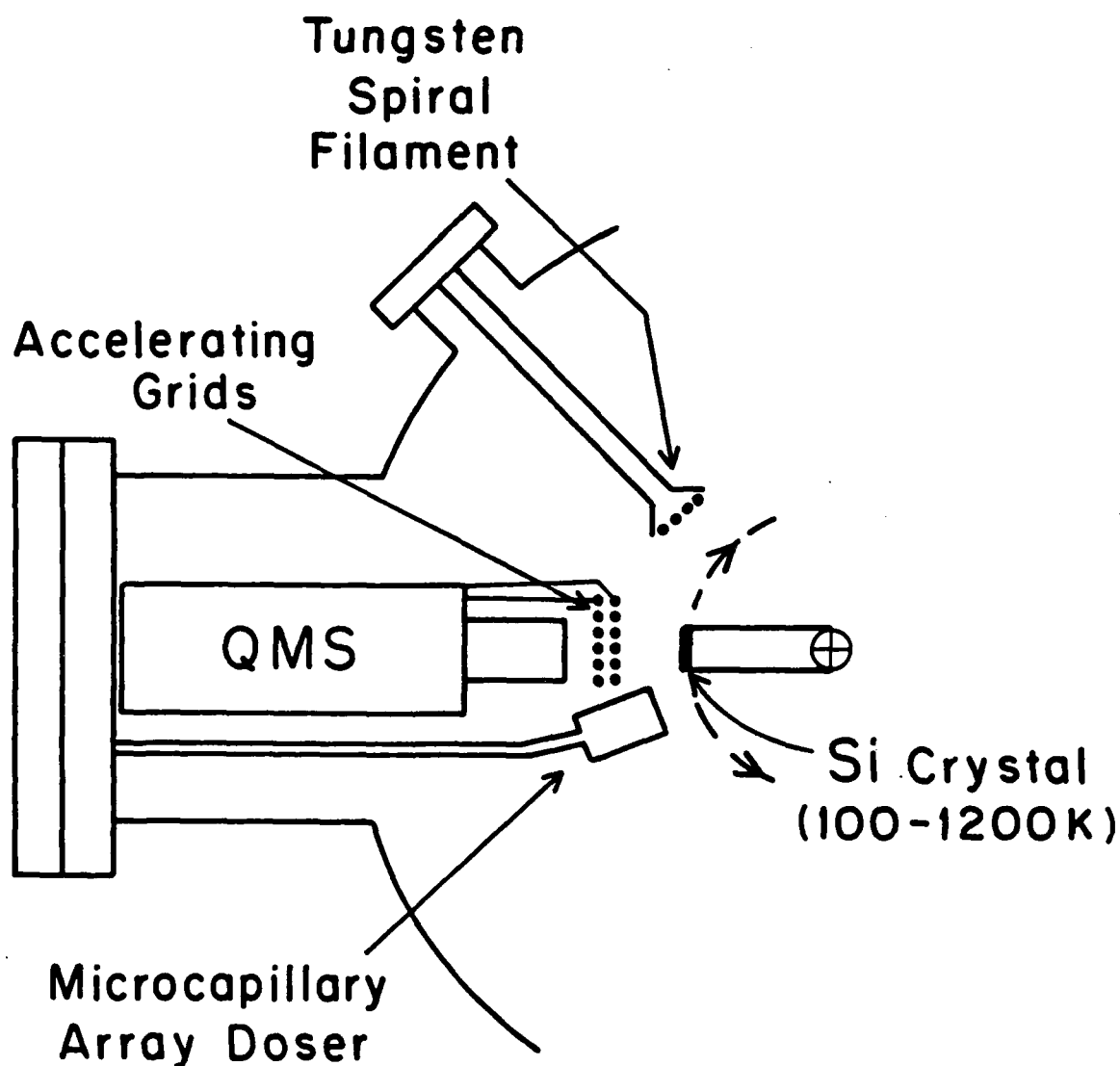
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Figure Captions

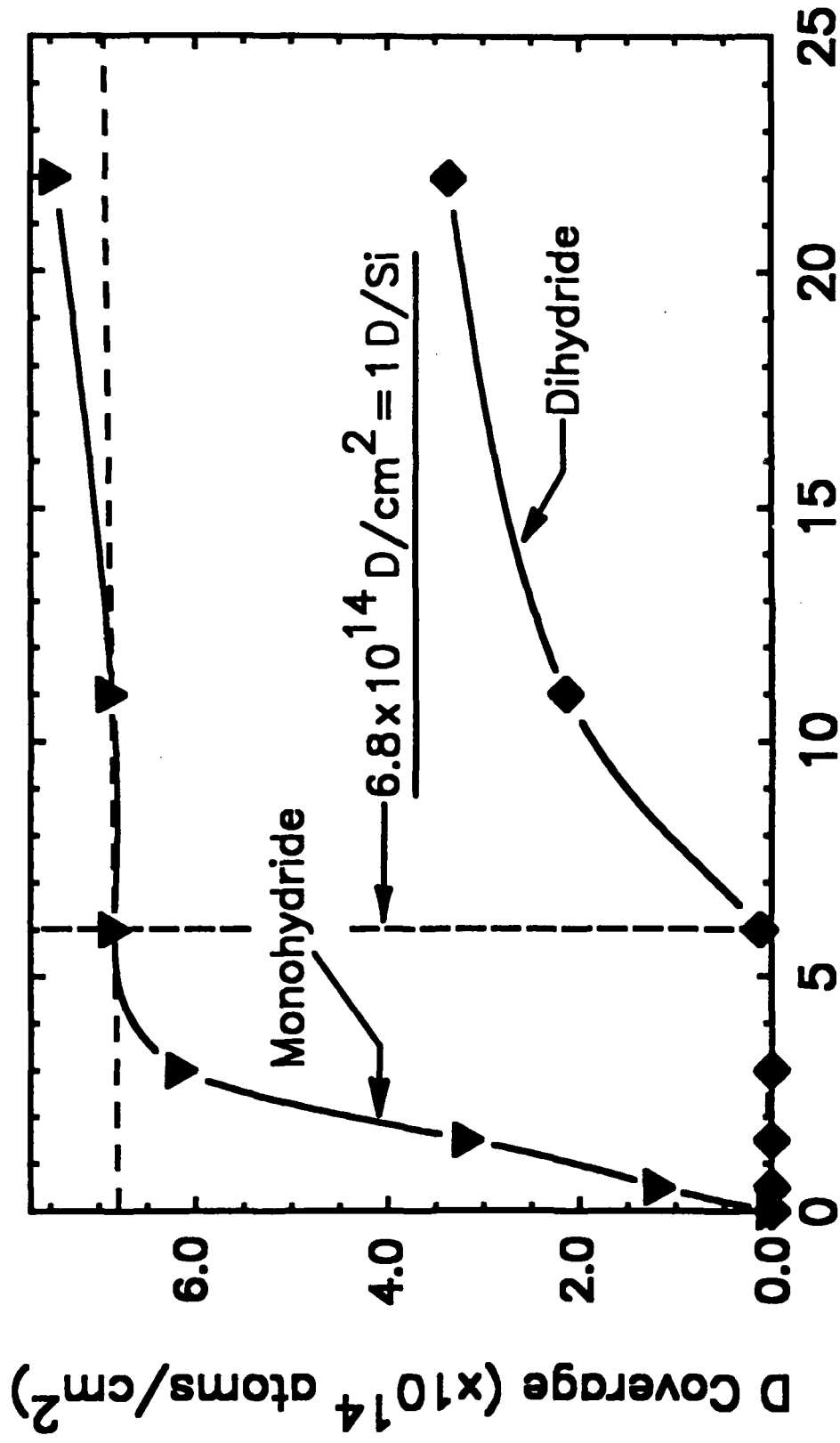Figure 1. Cut-away view of UHV system used for these studies. Base pressure: 4×10^{-11} Torr.

Figure 2. Calibration of D(a) coverage obtained from the sequential development of the D_2 desorption features from D(a) on Si(100)-(2x1). The x-axis corresponds to the D_2 exposure in Langmuirs (uncorrected) (1L = 1×10^{-6} Torr-sec) to the W-spiral D· source.

Figure 3. Adsorption kinetic experiment for NH_3 for different pre-adsorbed coverages of D(a) on Si(100).

Figure 4. Thermal desorption spectra observed for ammonia adsorbed on 0.81 D/Si on Si(100) at 120 K. A) ammonia species, B) hydrogen species.

Figure 5. Yield of the various isotopic ammonia desorption species at different D(a) coverages. Note that NH_2D predominates over the _entire range_ of D(a) coverage compared to NHD_2 and ND_3. This indicates that NH_2(a) is the predominant dissociation product for NH_3 on Si(100) in the temperature range 120 K - ~ 600 K.

Ultrahigh Vacuum Apparatus for Silicon Surface Chemistry

Tungsten Spiral Filament

Accelerating Grids

QMS

Si Crystal (100–1200 K)

Microcapillary Array Doser

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Figure

Deuterium Atom Coverage Calibration – Si(100)–(2x1)

D Coverage ($\times 10^{14}$ atoms/cm^2)

D$_2$ Exposure (Langmuirs, uncorrected)

6.8×10^{14} D/cm^2 = 1 D/Si

Monohydride

Dihydride

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Figure 2

D–Atom Blockage of NH_3 Adsorption on Si(100)

T_{ads}=120K

Crystal Rotated into NH_3 beam

NH_3 beam on

1.41

1.16

1.16   0.99

0.81

0.18

0.0

D coverage

D/Si

ΔP_{NH_3} (a.u.)

1.0

0.5

0.0

Time (s)

0   100 200 300 400 500 600 700 800 900 1000
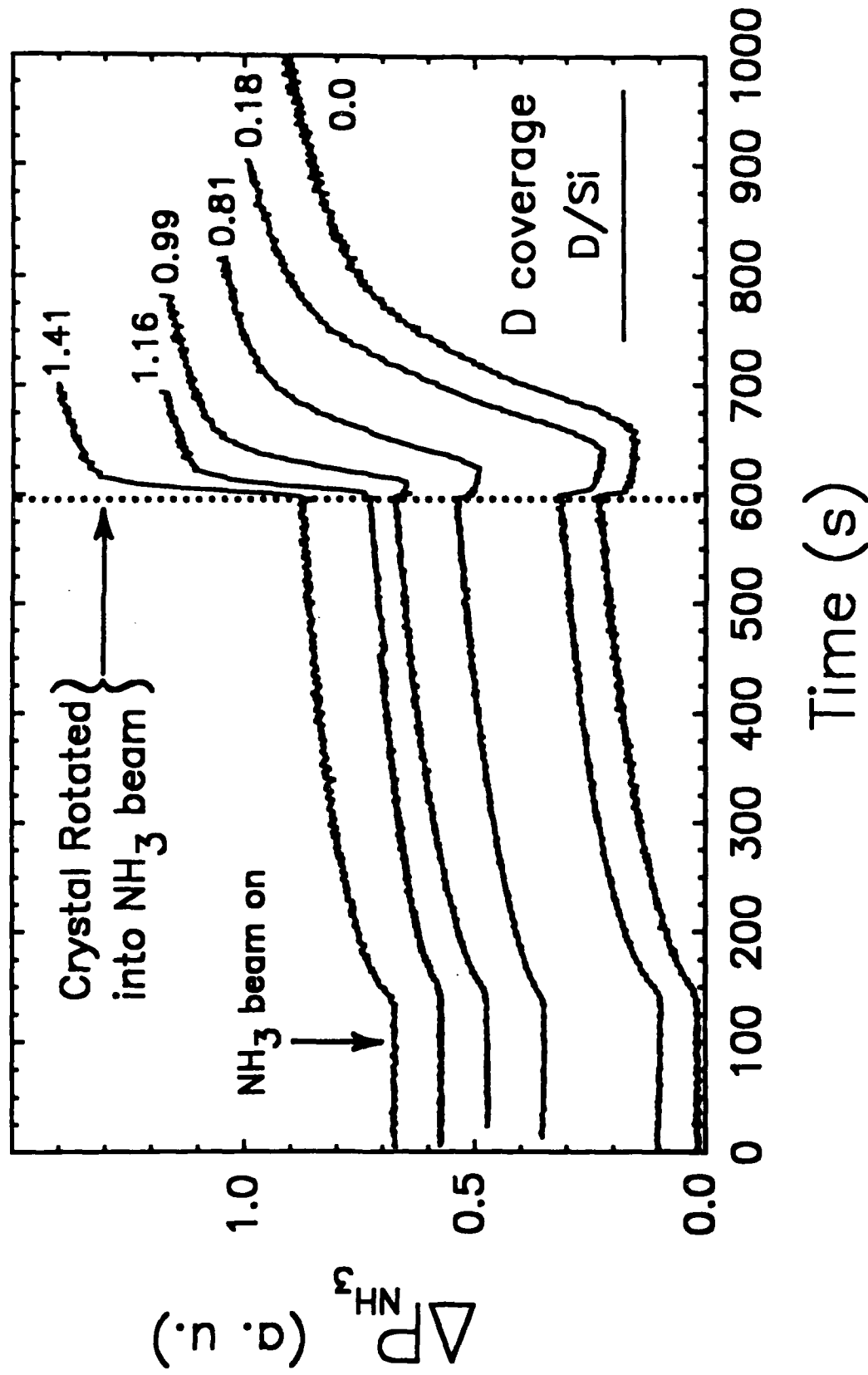
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Figure 3

Thermal Desorption from Ammonia Coadsorbed on D/Si(100)

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Figure 4
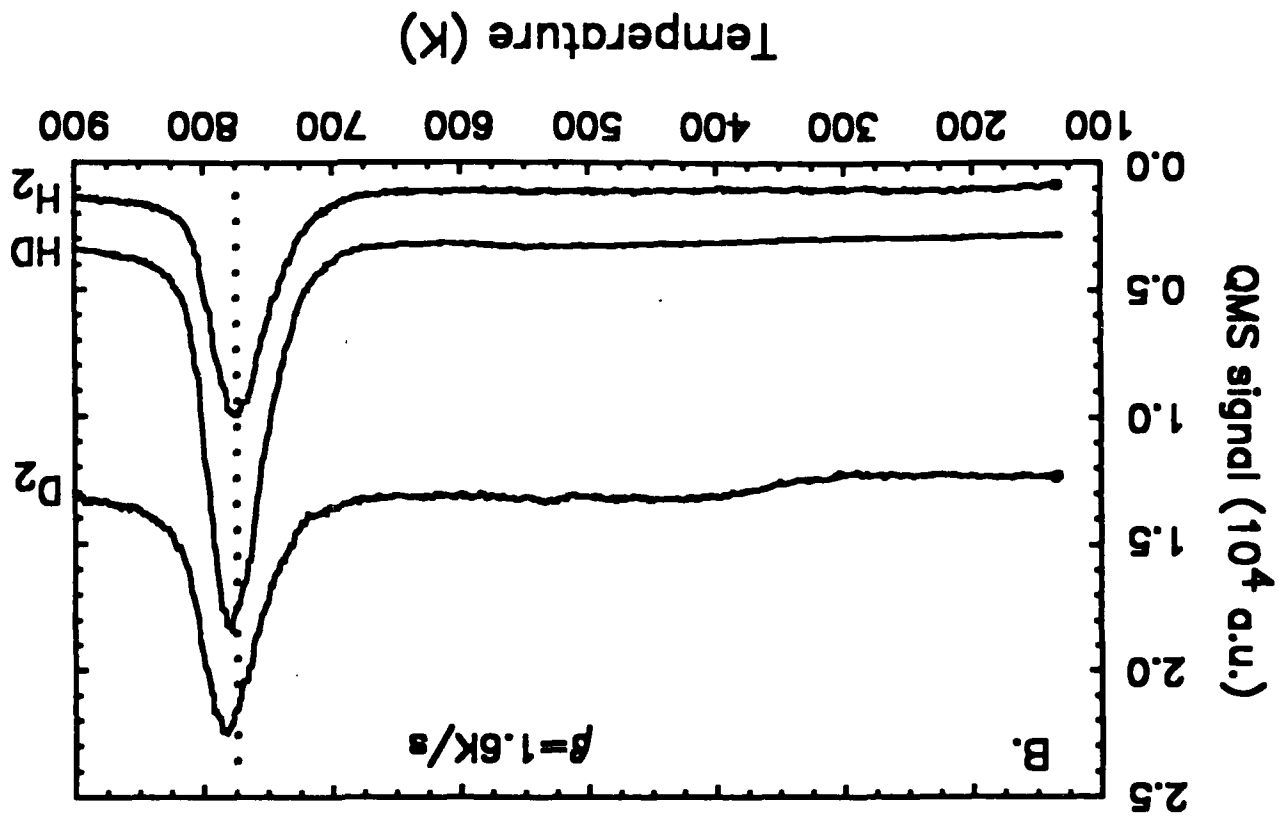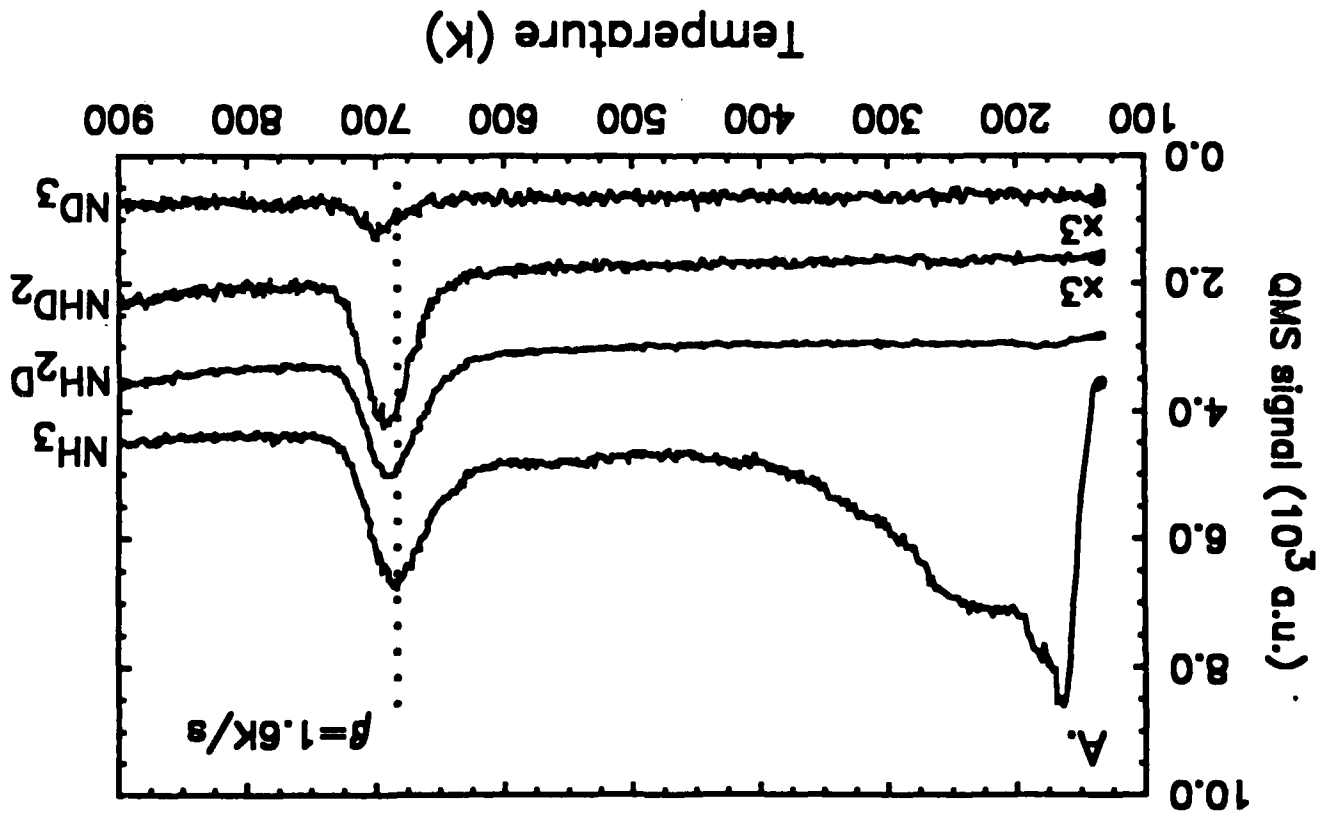
Distribution of Thermal Desorption Products from $NH_3/D·/Si(100)$

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Figure 5
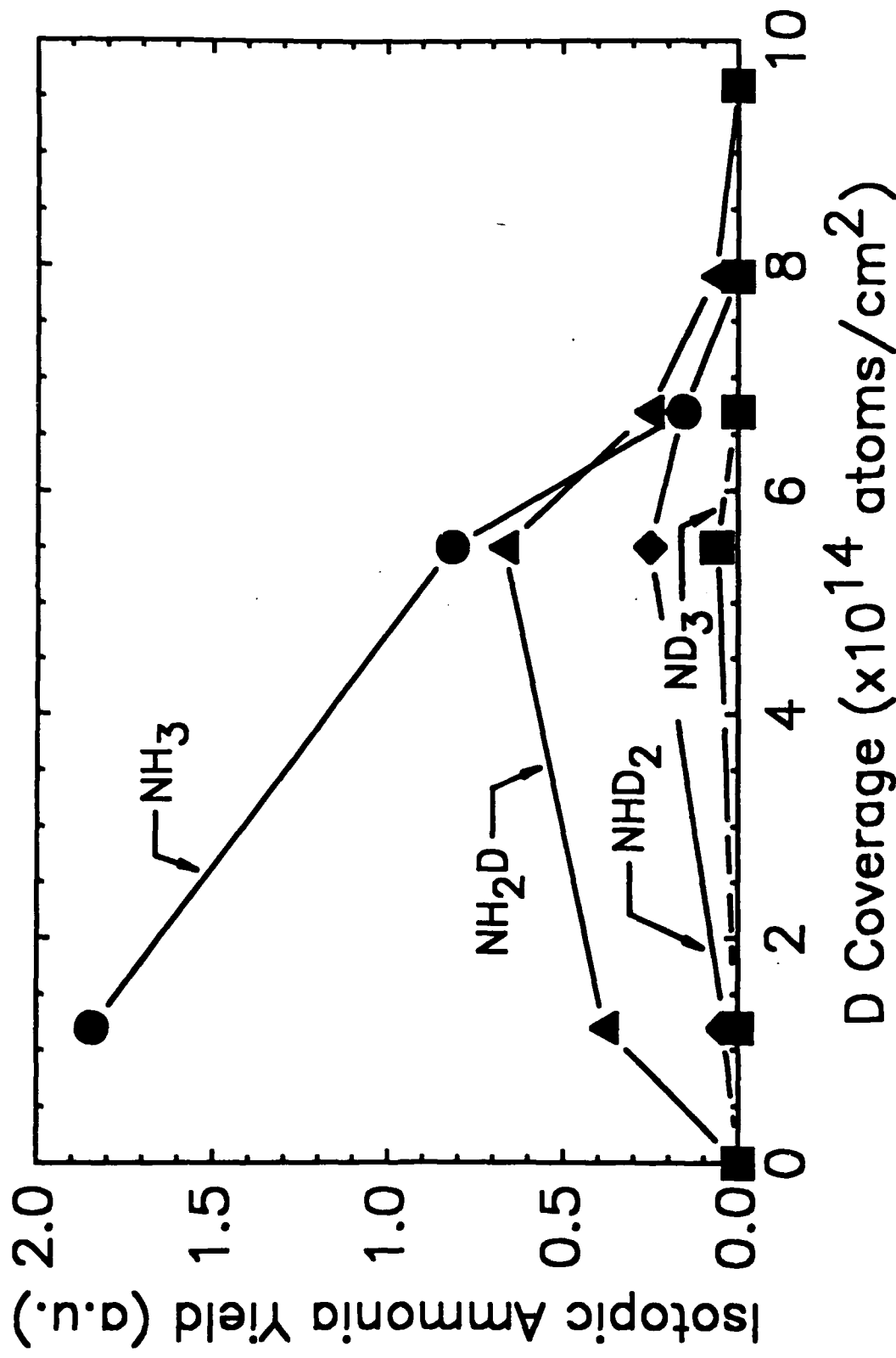
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