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Spectroscopy and Reactions of Hydrazoic Acid on Silicon Single Crystal Surfaces. (II). HN_3 and DN_3 on Si (100)

by

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Spectroscopy and Reactions of Hydrazoic Acid on Silicon Single Crystal Surfaces. (II). HN_3 and DN_3 on Si (100)

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ABSTRACT

Hydrazoic acid (HN_3) was employed for the first time as a nitrogen source for nitridation of Si surfaces. Its spectroscopy and reactions on different low Miller index surfaces have been investigated with XPS, UPS (X-ray and ultra-violet photoelectron spectroscopy), AES (Auger electron spectroscopy) and HREELS (high resolution electron energy loss spectroscopy) at temperatures between 120 and 1350 K. This study focuses on the spectroscopy and reactions on the Si(100) surface. HN_3 was found to adsorb molecularly on these surfaces since all molecular vibrational peaks such as the HN-NN stretching vibration at 150 meV, the HNN=N stretching vibration at 270 meV and the H-N_3 stretching vibration at 415 meV could be clearly observed by HREELS. These assignments were confirmed by an isotopic study using DN_3.

Warming the surface from 120 to 250 K caused HN_3 to desorb as well as to decompose into N_2 and NH, which further dissociated to produce N and H as the surface was annealed from 580 to 800 K. The presence of H adatoms was revealed by the appearance of the Si-H stretching vibration at 267 meV. At $T_s > 800$ K, H atoms began to desorb, while N remained on the surface forming Si_3N_4 at $T_s \cong 1350$ K. These observations were fully corroborated by UPS, XPS and AES data. The results of AES and UPS analyses also indicate that nitrogen could diffuse into the bulk of Si (100), similar to the Si(110) case.

KEYWORDS: Silicon (100); Hydrazoic acid; Nitridation; Characterization.

1. INTRODUCTION

Silicon nitride (Si_3N_4) has been employed in a variety of semiconductor processing procedures and devices, such as oxidation mask, diffusion barries and annealing caps, among others (1). The most commonly used compound for silicon nitridation is ammonia, which is very stable and usually requires high temperature or enhancement with electrical discharge or lasers (1,2).

In this series of studies, we have explored the applicability of hydrazoic acid which, unlike hydrazine, can be prepared with high purity and is chemically more labile than NH_3 and N_2H_4. The dissociation energy of the HN-N_2 bond is about 380 kJ/mole weaker than that of the H-NH_2 bond (3). This allows us to lower the processing temperature and also eliminate the need for external activations with lasers or electrical discharges.

In our preliminary study of the thermal stability of HN_3 on Si(110) between 120 and 1350 K, characterized by UPS and HREELS, we have found that HN_3 started to dissociate into NH and N_2 at temperatures as low as 220 K (4). The NH species dissociated further to produce N and H as the surface was annealed from 580 to 800 K. The H adatom, which appeared distinctively with the Si-H stretching vibration at 256 meV, began to desorb at $T_s >$ 800 K, with the remaining Si_xN species transformed into Si_3N_4 at $T_s \cong 1350$ K. This decomposition mechanism was fully corroborated by the results of UPS and HREELS analyses (4).

In the present work, we have carried out a detailed study on the spectroscopy and decomposition mechanism of HN_3 and DN_3 on Si(100) using UPS, XPS and HREELS. The result of this study is presented herein and compared in some detail with the Si (110) data (4).

2. EXPERIMENTAL

The experiment was carried out in an ultra-high vacuum (UHV) system with multiple surface diagnostics, which include XPS, AES, UPS, HREELS and LEED (low energy electron diffraction) (4). The UHV system, which has a base pressure of about 5×10^{-9} Pa, consists of four different compartments: preparation/deposition, XPS/UPS/AES, LEED and HREELS. Surface samples can be directly transferred from the prep-chamber to other analysis compartments via interlocks under UHV conditions.

The HREELS spectroscopic measurement was performed with an electron beam having the primary energy of $E_p = 5$ eV. The resolution was ΔE (FWHM) $\cong 7$ meV in the straight through mode. Angular dependence could be studied by rotating the movable energy analyzer around the axis perpendicular to the incident plane of the e-beam.

The UPS and XPS measurements were carried out with He II at 40.8 eV and Al $K_{\alpha 1,\alpha 2}$ at 1486.6 eV, respectively. Both analyses were made with a 180° hemispherical electrostatic condenser analyzer for electron detection.

Si(100) samples, obtained from Virginia Semiconductor Co. as highly polished discs, were cut into $1.5 \times 1.0\ cm^2$ chips. These chips were cleaned with dilute hydrofluoric acid solution and then rinsed with de-ionized water. The mounted Si(100) sample was further cleaned by repeated annealing at $T_s > 1470$ K until no detectable C, N and O by XPS, AES and HREELS.

HN_3 and DN_3 were prepared by acidification of NaN_3 (Aldrich) with 60% H_3PO_4 and D_3PO_4, respectively. Both forms of phosphoric acid were also purchased from Aldrich with purities greater than 99%. The generated hydrazoic acid was purified through a chain of cold traps maintained at 195 K (dry ice), 160 K (ethanol slush) and 77 K (liquid N_2) under constant diffusion-pumping. FTIR analysis of the purified sample showed no detectable impurities. From this analysis, the DN_3 sample was found to have about 95% D-enrichment.

3. RESULTS and DISCUSSION

3.1 HREELS

Figure 1 shows a series of HREELS spectra taken from a 2.5 ± 0.5 L (Langmuir) HN_3 dosed Si(100) sample at 120 K and annealed at the indicated temperatures. When dosed at 120 K, peaks at 56, 153 (shoulder), 163, 272 and a broad weak peak at ~415 meV were observed. By analogy to earlier IR/Raman studies (5,6), these peaks can be assigned to the different modes of molecular vibrations as shown in Table 1. The good agreement between the IR/Raman and our HREELS spectra suggests that HN_3 molecules were essentially associatively adsorbed on the surface. However, the peak at 56 meV and the broad peak at ~415 meV may imply the formation of the dimers to some extend upon adsorption because of the relatively high dosage employed in the present work. The 56 meV peak may have contribution from the H-bond torsion vibration in dimer at 48 meV besides the two N_3 bending vibrations and the 415 meV peak may have contributions from N-H stretching vibrations at 394 and 411 meV, as observed in HN_3 dimers (6).

When the sample was annealed at 520 K, the following changes were observed. Firstly, all peak intensities were attenuated by more than two times, which obviously suggests the partial desorption of the adsorbed species. In addition, the peak at 58 meV shifted to 77 meV and the peak at 415 meV shifted to 428 meV with its FWHM being significantly reduced. These changes are probably mainly due to the breaking of the dimers. Furthermore, since a peak at 422 meV was observed for NH_x species adsorbed on Si substrates (7,8), the peak at 428 meV observed here, together with the appearance of a new peak at 110 meV due to Si-NH_x stretching vibration, also suggests some cracking of the HN-NN bond and thus forming the adsorbed NH_x species. This HN-NN bond cleavage was essentially complete when the surface was annealed at 610 K. At this temperature, all HN_3 molecular vibration peaks were absent, the spectrum was dominated by a broad peak at 110 meV due to different bonding between Si and NH_x (9-12). Meanwhile the new peak at 267 meV due to the Si-H stretching vibration indicates the dissociation of some N-H species. The latter was further confirmed by the spectrum recorded after annealing the sample at 800 K, where 267 meV peak grew bigger and the N-H stretching vibration at 428 meV essentially disappeared.

Further annealing the sample to higher temperatures caused Si-N bonding structure change as evidenced by the shifting of the Si-N peak position and the variation in peak intensities.

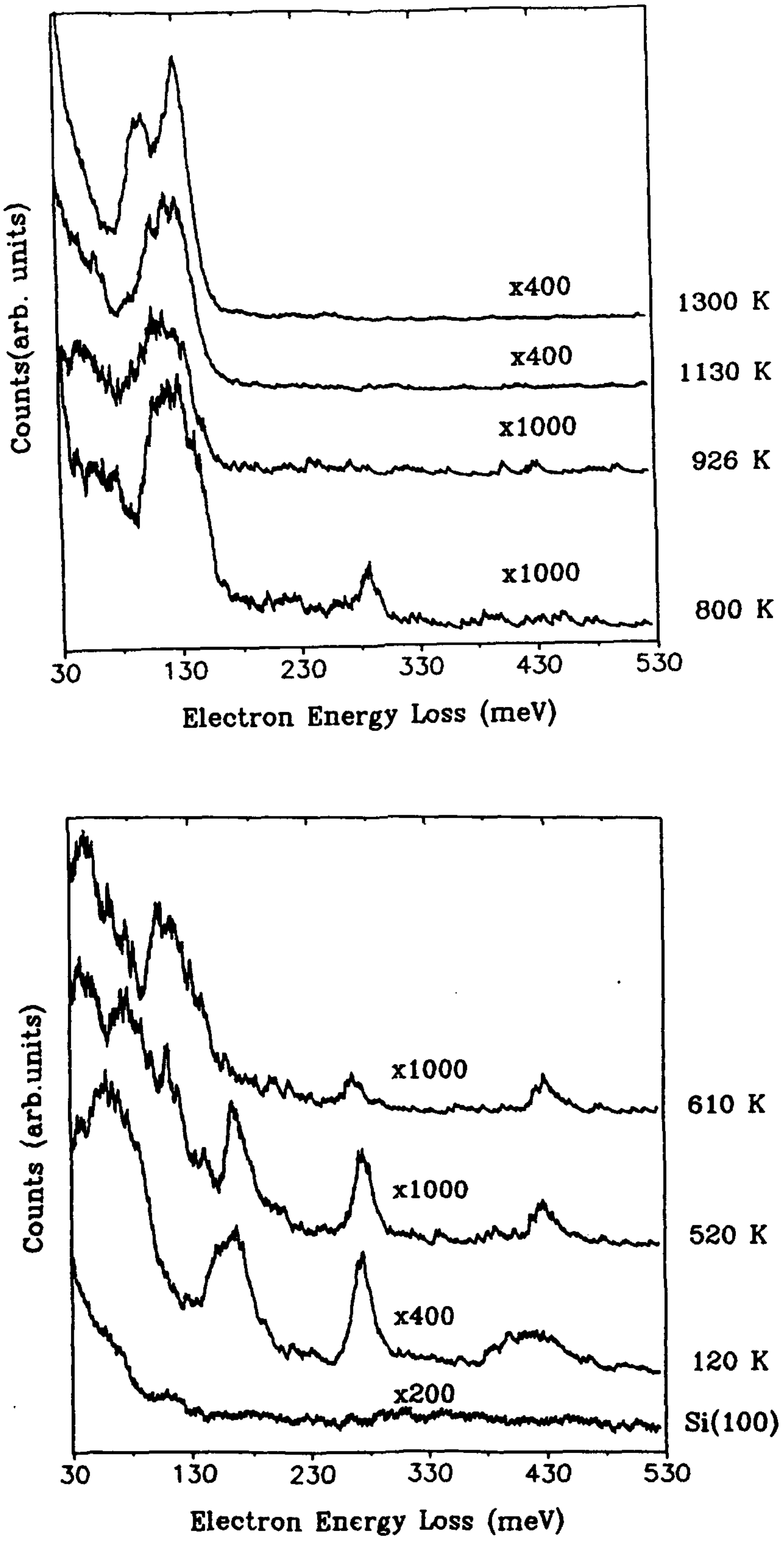

FIGURE 1. HREEL spectra of 2.5 ± 0.5L HN_3 dosed Si(100) recorded at 120 K after annealing at the indicated temperatures.

Similar peak shifting and intensity variation were also observed in the earlier IR (13) and HREELS (14, 15) studies of NH_3 on Si substrates.

A similar experiment was also carried out with DN_3 to confirm some of the HREELS peak assignments. As shown in Figure 2, upon dosing 2.5 ± 0.5 L DN_3 on Si (100) at 120 K, peaks at 60, 128, 153, 271 and a shoulder at ~300 meV were evident. The spectrum clearly shows the isotopic effect on the corresponding molecular vibration frequencies. Comparison of the peak assignments with those of IR/Raman spectra is also given in Table 1.

It should be point out that because of the fast hydrogen-deturium exchange on the walls of the chamber and inlet line, the corresponding HN_3 peaks also appeared in the DN_3 HREEL spectra. When the sample was annealed at various temperatures, essentially the same results as HN_3 on Si(100) were found, although the spectra were more complicated due to the existence of both HN_3 and DN_3 species on the surface. An additional spectrum after annealing at 250 K is also shown in Figure 2, which is nearly identical to that of the 520 K spectrum. Thus the annealing effect discussed above for HN_3 on Si(100) at 520 K should also apply to the spectrum at 250 K, if it were recorded. In fact, a similar annealing effect was found for HN_3 on Si(110) at as low as 220 K (4).

3.2. UPS

Figure 3 shows the temperature dependence of UPS spectra of 2.0 ± 0.5 L HN_3 dosed Si(100). When dosed at 120 K, UPS (He II) spectra exhibited peaks at 4.7, 6.7, 8.9 eV below E_F. In addition, a shoulder at 10.3 eV with a long tail extended to the higher binding energy (B.E.) side was also visible. By comparing with the gaseous HN_3 UPS results (16),

Table 1. Vibrational frequencies (in meV) and assignments for HN_3 and DN_3 in the gas phase and on Si surfaces.

Vibrational Mode	Gas^a		Si(100)^b		Si(110)^c	
	HN_3	DN_3	HN_3	DN_3	HN_3	DN_3
δ (N_3)	66	61	56	60	55	—
δ (N_3)	75	73	—	—	77	73
υ (HN-N_2) ; (DN-N_2)	143	147	153	153	150	158
β (H-N) ; (D-N)	157	118	163	128	160	128
υ (HN_2=N) ; (DN_2=N)	265	262	272	271	265	270
υ (N-H) ; (N-D)	414	307	415	300	414	307

a. Refs. (5) and (6). b. This work. c. Ref. (4)

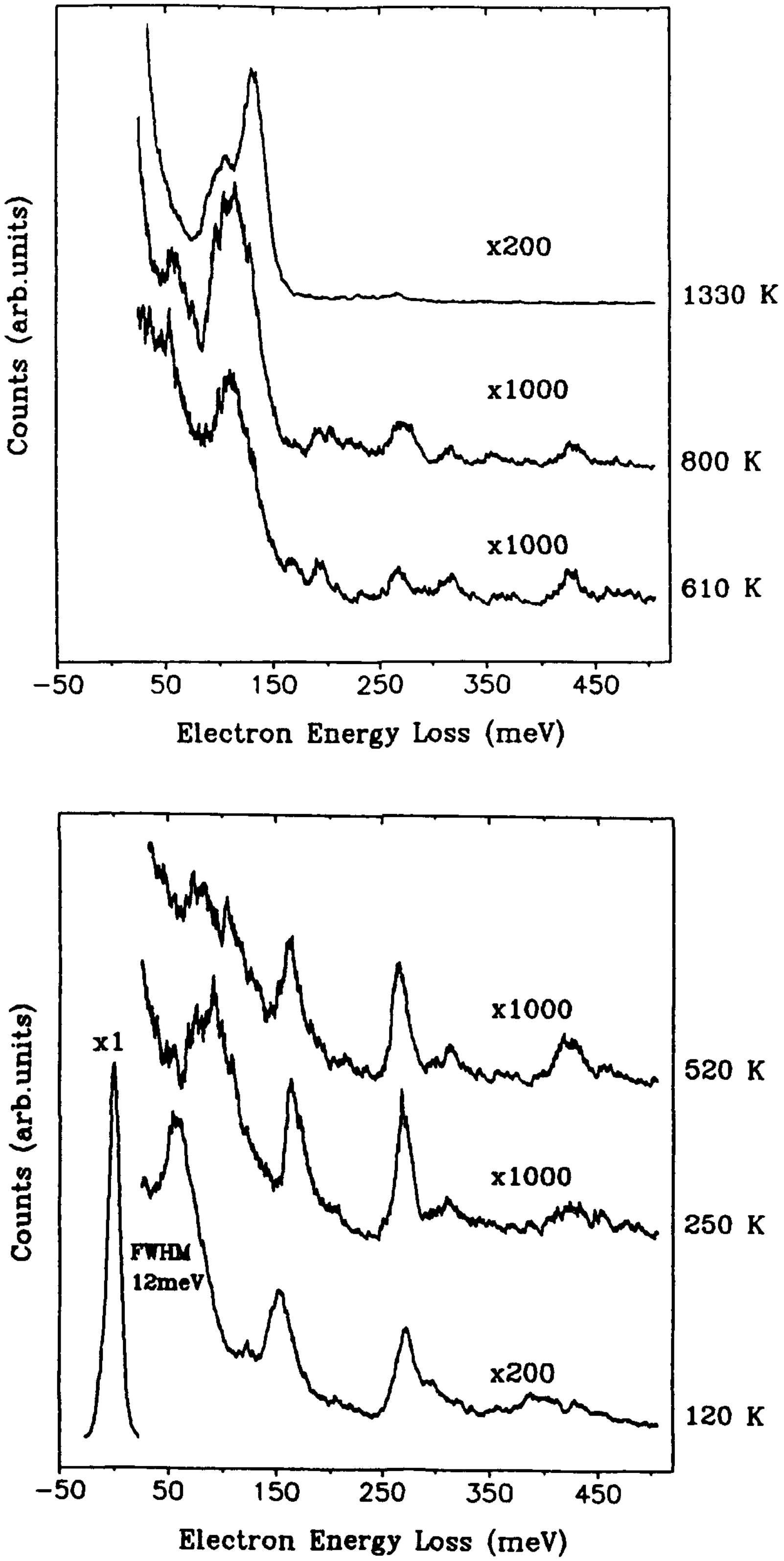

FIGURE 2. HREEL spectra of 2.5 ± 0.5 L DN_3 dosed Si(100) recorded at 120 K after annealing at the indicated temperatures.

these peaks can be assigned to the 2a", 9a' and 8a' molecular orbitals and the shoulder at ~10.3 eV to the 7a' orbital. The tail in the spectra should be due to the 1a" and 6a' molecular orbitals, respectively.

When the surface was annealed at 520 K, the peaks at 4.7 and 8.9 eV were attenuated. On the other hand, the peak at 6.7 eV was enhanced and shifted to ~6.9 eV. Additionally, a new peak at 12.1 eV appeared. The peak intensity attenuation at 4.7 and 8.9 eV reflects the partial desorption of the adsorbed species, while the 6.7 and 12.1 eV peak enhancement suggests the formation of the Si-N bond due to the dissociation of HN_3 molecules, since Si-NH_x species were found to show peaks at the similar energy positions. The energy separation of 5.2 eV between the two peaks observed here agrees very well with those of UPS results for a SiN_x:H (x=1) film (17) and an NH_3 dosed Si(111) sample (18). In the latter case, NH_3 molecules were believed to be dissociatively adsorbed on the surface and the energy separation between the two UPS peaks ranged from 5.25 to 5.7 under different experimental conditions.

Further annealing the sample from 620 to 950 K caused a shrinking of the 12.1 eV peak due to the N-H bond (19) and a further enhancement of the peak at ~7 eV. These changes can be attributed to the cracking of the N-H bond and further formation of the Si-N bond, in consistence with our HREELS observation in the same temperature range. The UPS spectrum recorded after annealing the sample at 1180 K was similar to that of the clean surface (dashed line) except the three noticeable humps at 4.5, 7 and 11.5 eV, respectively. On the other hand, HREELS and XPS results did not show any obvious N-signal attenuation by annealing the sample at the same temperature. Therefore the annealing effect observed in the 1180 K UPS spectrum as well as the AES result, which also showed an N-signal intensity decrease at high annealing temperatures, suggests the occurrence of N-atom diffusion into the subsurface so that they cannot be detected effectively by the UPS and AES techniques. Similar observations were made in the case of HN_3 on Si(110) (4) and were also reported by Taguchi et al. (14) and Avouris et al. (20) in the nitridation of Si(100) surfaces. However, in an on-going study of HN_3 on Si(111), a very strong UPS peak at 7.5 eV, due to SiN species, persisted after the sample was annealed at similar temperatures (21). Finally, it should be pointed out that the three humps at 4.5, 7 and 11.5 eV compare favorably with UPS results taken from Si_3N_4 samples (19,22).

3.3 XPS

Figure 4 shows a series of XPS spectra taken by dosing 2.0±0.5 L HN_3 on Si(100) at 120 K and then annealing the sample at the indicated temperatures. At 120 K, peaks at 404.7 and 400.8 eV with FWHM's of 3.8 and 2.5 eV, respectively, were observed; these peaks correlate well with the XPS results taken from solid HN_3 samples by Lee et al. (16). The peak at 404.7 eV is due to the central N atom, while the peak at 400.8 eV with a larger

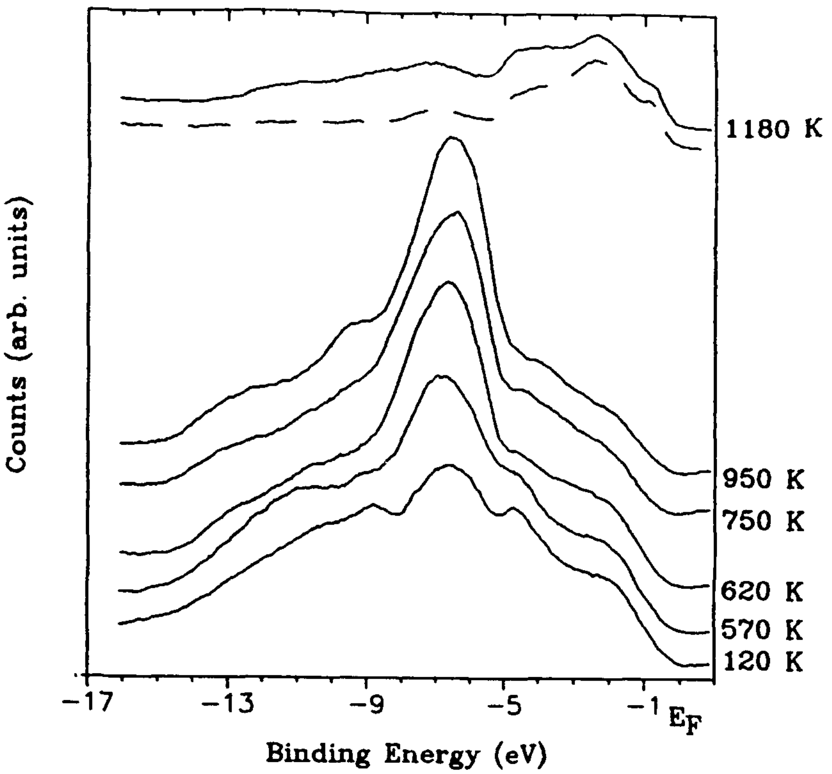

FIGURE 3. UPS spectra of 2 ± 0.5 L HN_3 closed Si(100) recorded at 120 K after annealing at the indicated temperatures.

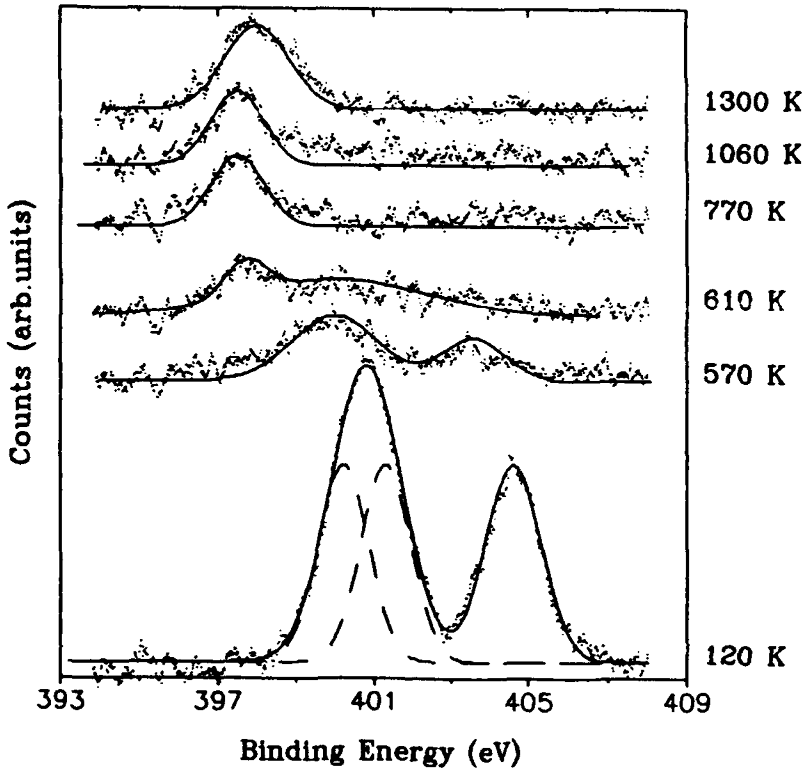

FIGURE 4. XPS spectra of 2 ± 0.5 L HN_3 dosed Si(100) recorded at 120 K after annealing at the indicated temperatures.

FWHM, is due to the two terminal N atoms. These two terminal N atoms have different atomic charges (16, 23) in HN_3 molecules, thus the peak can be deconvoluted into two peaks (with equal intensity and FWHM) at 400.2 and 401.2eV, as shown in Figure 4 by the dashed curve.

As the sample was annealed at 520 K, all peaks were significantly attenuated, broadened and shifted toward the lower B.E. side. The peak intensity decrease is obviously due to the desorption of the adsorbate, while the peak broadening and shifting may be due to the following possibilities. Firstly, the partial dissociation of the HN-NN bond as well as the breaking of the dimers possibly existed at 120 K as discussed in the HREELS section. The broad peak centered at 399.8 eV should have contributions from NH species, which was expected to show a peak at 399 eV (18), and the breaking down of dimers, i.e. the disappearance hydrogen bonding also tends to shift the N peaks towards lower B. E.'s (24). Secondly, charging-effect change due to desorption and dissociation of the adsorbate could also cause the N XPS peaks shift. Thirdly, the possibility of N_3 species formation, due to the breaking of the H-N_3 bond, may be induced by X-ray irradiation. The X-ray induced H species desorption and N-H stretching vibration peak intensity attenuation, because of the breaking of the H-N bond, was noted in both NH_3 (25) and N_2H_4 (8) adsorbed on Si(111). To the best of our knowledge, there is no N_3 XPS information available at the present time; however, the XPS spectrum of N_3^- negative ions does show a shift towards the lower B.E. side for both N peaks as compared to those of HN_3 XPS (16).

At 610 K and above, only one major peak at 397.5 eV was evident, which, according to previous studies (19, 26, 27), is due to atomic N on Si substrates; this indicates the formation of Si-nitride following the dissociation of the N-H bond. The tail at the higher B.E. side of the 397.5 eV peak in the 610 K spectrum is due to the incompletely dissociated NH species. Finally, at 1300 K the peak shifted back to 397.7 eV, indicating the change in the Si-N bonding structure and the diffusion of N atoms into the subsurface to form Si-nitride insulating layers (19).

4. CONCLUSIONS

When 2.5 L HN_3 was dosed on a Si(100) surface at 120 K, the molecules were found to be molecularly adsorbed on the surface with possible formation of dimers to some extent. HREELS study of DN_3 was also carried out to confirm some of the EELS peak assignments. Upon annealing the sample at 250 K, HN_3 started to dissociate into N_2 and NH species accompanied by partial desorption. The HN-NN bond breaking was essentially complete at $T_s > 620$ K. Further annealing the surface caused the breaking of the N-H bond, the desorption of H species and the formation of Si-nitride. At $T_s > 1000$ K, the significant attenuation of N signals in UPS and AES spectra, but not in HREELS and XPS spectra, suggests that N atoms can readily diffuse into the Si(100) substrate. These results were essentially the same as those observed in our recent study of HN_3 (DN_3) on Si (110).

5. ACKNOWLEDGMENT

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