

Surface Science 301 (1994) 118-128

The 308 nm laser photodissociation of HN_3 adsorbed on Si(111)-7 × 7

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(Received 11 May 1993; accepted for publication 13 August 1993)

Abstract

The photodissociation of HN₃ adsorbed on Si(111)-7 × 7 at 308 nm was investigated using HREELS and XPS. Species such as NH_x , N_2 , and N_3 , were identified on the surface with comparable concentrations after the irradiation with 1×10^{20} photons of a 10 L HN₃ dosed Si(111) surface. The N₃ species showed two stretching modes at 178 and 255 meV, while that of the N₂ appeared at 206 meV in HREELS. The formation of these products was also corroborated by the corresponding XPS results. Further laser irradiation caused the dissociation and partial desorption of the adsorbates with NH_x left on the surface. Annealing the post-irradiated sample to 500 and 800 K resulted in the breaking of the NH bond and the desorption of the H-species, while the atomic N remained on the surface forming silicon nitride. The possibility of using HN₃ for laser-induced chemical vapor deposition of Si₃N₄ and group-III nitrides at low temperatures is suggested.

1. Introduction

The thermal decomposition of N-containing species, such as NH_3 , N_2H_4 and HN_3 on Si substrates has been studied extensively [1–19] using different surface sensitive techniques including high-resolution electron energy loss spectroscopy (HREELS), ultraviolet photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). On both Si(111)-7 × 7 and Si(100)-2 × 1 surfaces,

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NH₃ was found to dissociatively adsorb on the substrates at $T \approx 80$ K. Further thermal treatment caused continuous NH bond breaking, although the NH₂ species behaved differently on the two surfaces [10]. Above 800 K, the dissociation of NH_x species and the desorption of H₂ were complete, with only the atomic N left on the surface forming Si nitride. Partial dissociation of the NH bond also occurred upon the adsorption of N₂H₄ on Si(111)-7 × 7 at 120 K [15]. In this case, the N–N bond started to break at above 600 K. Similar results were also found for HN₃(DN₃) on Si substrates; however, the HN–NN bond breaking occurred at lower surface temperatures [16–19].

On the other hand, very few studies on the photodissociation of these N-hydrides on Si sur-

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faces have been reported, although numerous studies on their photodecomposition reactions in the gas phase have been made [20-24]. Surface photolysis is a complicated physico-chemical process; according to several recent reviews [25-28], the photodissociation of adsorbates could be induced both thermally and nonthermally. In the former process, the surface is heated either through direct absorption of photons by the substrate or through energy dissipation from the relaxation of excited adsorbates. In a nonthermal process, the photodissociation could be caused by the direct interaction between adsorbates and photons or photo-generated hot carriers from the substrate. In this paper, we report nonthermal photodissociation of HN₃ adsorbed on Si(111)- 7×7 at 100 K under the irradiation of 308 nm excimer laser. In contrast to the results of the thermal decomposition of HN₃ on Si(111)-7 \times 7 [18], both N_2 and N_3 were identified in addition to the more stable NH, species after the irradiation of a 10 L HN₃ dosed sample with 1×10^{20} photons. The N_3 and some NH_x species are likely produced by the secondary reactions occurring on the surface. These results are also different from those of gaseous HN_3 photolysis [20–24], which produces exclusively N₂ and NH($^{1}\Delta$) in the UV region, although the product $NH(^{1}\Delta)$ is at different internally excited states and the N₂ and $NH(^{1}\Delta)$ yields are slightly different when different wavelength photon beams are applied.

2. Experimental

The experiment was carried out in a customdesigned UHV system with a base pressure of $< 1 \times 10^{-10}$ Torr as described elsewhere [16–19]. Both the Si(111) surface and the gaseous HN₃ sample were prepared in the same manner as described in Ref. [18]. A Mg X-ray source was used for the XPS measurements with a pass energy setting at 50 eV to give a resolution ≤ 1.3 eV full width at half maximum (FWHM), the value obtained for the N1s XPS taken from a well-prepared Si₃N₄ sample. In the HREELS measurements, an electron beam with a primary energy of 5 eV and FWHM of 6 meV in the straight-through mode was used. An excimer laser (Lambda Physik EMG-102) was operated at 308 nm wavelength with a repetition rate of 5 Hz. The photon beam covers the whole surface area with a typical laser fluence of about 20 mJ/ $cm^2 \cdot pulse (3 \times 10^{16} photons/cm^2 \cdot pulse)$ on the surface. The surface temperature rise under the experimental conditions could not be measured. but it should be insignificant, because no noticeable desorption or decomposition of HN₃ was observed after irradiating the sample with a few tens of laser shots. In our earlier study of the thermal decomposition of HN₃ on Si(111)-7 \times 7 [17], we detected a significant amount of desorption and decomposition of HN₃ when the surface was warmed from 120 K to the vicinity of 200 K.

After the sample was dosed with a desired amount of HN_3 on the surface at 100 K and analyzed with HREELS and XPS, it was moved to a port with quartz window (>95% transmission for 308 nm light) for laser irradiation at normal incidence. The irradiated sample was immediately moved back into the analysis chamber for HREELS and XPS measurements.

3. Results

3.1. HREELS

When 10 L HN₃ was dosed on Si(111)-7 \times 7 at 100 K, HREELS produced peaks at 60, 150, 266 and 388 meV as shown in Fig. 1. As discussed earlier in Ref. [17], these peaks are due to the monomeric, dimeric and/or polymeric HN₃ adsorbed on the surface. The 150 meV peak is a combination of the NH deformation and HN-NN stretching modes, expected to be at 143 and 157 meV, respectively. In addition, all bands observed here should be the convolution of a few peaks from the corresponding monomeric, dimeric and/or polymeric HN₃ species. In an IR study of HN_3 in solid N_2 , these peaks could be resolved and identified [29]. With the increasing concentration of HN_3 in N_2 , the relative intensities of the lower frequency bands increased, particularly the N_3 deformation and the NH stretching modes, because of the increased formation of dimeric

and/or polymeric HN_3 . Unfortunately, these peaks could not be resolved in HREELS with the resolution used in the present study. However, we did observe a gradual red-shift of the peak positions as the HN_3 dosage was increased (see Fig. 1).

When the 10 L HN₃ dosed Si(111) was exposed to 308 nm excimer laser irradiation, the following changes were noted as shown in Fig. 2, indicating the formation of NH_x (x = 0,1,2), N₂ and N₃ species on the surface. The NH species was clearly indicated by the appearance of the new peak at 113 meV and by the broadening and the blue-shifting of the 388 meV peak, which had a considerable contribution from the 421 meV component. The latter peak was observed earlier in the studies of NH₃ and N₂H₄ on Si(111) after the partial breaking of NH and NN bonds; the peak was attributed to the NH_x (x = 1, 2) species [10,15]. The N₂ species, on the other hand, was



Fig. 1. The HREELS of HN₃ on Si(111)- 7×7 at 100 K and at 0.3 (bottom) and 10 L (top) dosages. Note the red-shift of all peaks except that at 265 meV.

evidenced by the appearance of 206 meV peak. For N_2 adsorbed on metal surfaces, the NN stretching mode was found to range from 180 to 277 meV, depending upon the N_2 adsorption geometry [30–33].

As to the N₃ species, it may be related to the shift of the 150 and 266 meV peaks to 178 and 255 meV, respectively, because peaks at 167–171 and 253–264 meV were observed in IR for azide ions [34–36]. The blue-shift of the N–NN and the red-shift of the NN \equiv N stretching modes should be expected, since electrons in π bonds delocalize across the whole N₃ radical after the dissociation of the N–H bond. N₃ formation was further confirmed in our XPS results discussed below. Finally, the remaining peak at 390 meV indicates that a small amount of HN₃ molecules survived on the surface.

Further laser irradiation caused additional dissociation and also induced a partial desorption of the N2, N3, and HN3 species. Resonance peaks at 178, 206 and 255 meV virtually disappeared, the NH stretching mode was narrowed and shifted to 422 meV and a new peak at 187 meV due to the NH₂ deformation mode was fully developed (see Fig. 2a). In addition, a shoulder at 140 meV attributable to the NH deformation vibration was resolved from its adjacent more intense peak at 113 meV. The latter peak, which has contributions from Si-NH, stretching, NH, rocking and Si₂NH bending vibrations [12], was also greatly enhanced by further laser irradiation. This HREEL spectrum is clearly dominated by the NH, (x = 0,1,2) species left on the surface.

When this post-irradiated sample was annealed at 500 and 800 K, further dissociation of the NH bond occurred on the surface, as indicated in Fig. 2b by the disappearance of the 140 and 187 meV modes due to the NH bending and NH₂ deformation vibrations, respectively, the attenuation of the NH stretching mode at 422 meV and the appearance of the Si–H stretching mode at 260 meV. This mode survived up to 800 K is probably due to the incorporation of atomic N into the Si lattice and thus increases the thermal stability of the Si–H species. The Si–H stretching mode was also observed in HREELS for other H-containing molecules, e.g., CH₃OH and NH₃

[2,37], on Si(111) after annealing the sample at $T_{\rm S} \ge 800$ K.

3.2. XPS

Fig. 3 shows the N1s XPS of HN₃ on Si(111)-7 × 7 at 100 K with the indicated dosages. The N1s signal is mainly composed of two peaks at 404.1 and 400.3 eV, originated from N¹¹ and N¹ plus N¹¹¹ atoms, respectively; where the superscripts denote the nitrogen atoms at different positions in the HN₃ molecule: HN¹N¹¹N¹¹¹. In Ref. [17] we reported that the broader and more intense peak at 400.3 eV can be deconvoluted into two peaks located at 400.8 and 399.8 eV with equal intensities and same FWHM's as illustrated in Fig. 3. These two peaks, derived from the N¹¹¹ and N¹ atoms, respectively, have an energy separation of 1 eV because of their different chemical environments. The results are consistent with those taken from HN_3 condensed on Au [38] and with those from an atomic charge calculation [39]. Furthermore, a minor peak at 398.1 eV can be deconvoluted from the 400.3 eV peak. This 398.1 eV component is attributable to the NH_x species, resulting from to the X-ray induced dissociation of HN₃.

Fig. 4 illustrates the effects of laser irradiation and thermal heating after the irradiation on the N 1s XPS signal of HN₃ on Si(111). Prior to laser irradiation, the N 1s XPS peak could be deconvoluted into at least four peaks derived from the HN₃ (three peaks) and the NH_x species as discussed above (see Fig. 4, spectrum a). When the 10 L HN₃ dosed sample was irradiated with $1 \times$ 10^{20} photons at 308 nm, four major peaks at 399.0, 401.5, 403.4 and 397.4 eV were present in the XPS (see Fig. 4, spectrum b).

The 399.0 and 403.4 eV peaks are identical to those of the XPS results taken from LiN_3 con-



Fig. 2. (a) The laser effect on HREELS of 10 L HN₃ dosed Si(111)-7 \times 7 at 100 K and (b) the thermal effect on HREELS of HN₃ on Si(111) after being exposed to 3×10^{20} photons.

densed on an Au surface [38]. The 403.4 peaks also have essentially the same FWHM's in both cases. However, the 399.0 eV peak is broader for N₃ on Si (FWHM = 1.92 eV) than that for LiN₃ on Au (~ 1.4 eV). Furthermore, the intensity of the 399.0 eV peak is more than twice that of the 403.4 eV peak for the irradiated HN₃ on Si(111), while the intensity ratio of these two peaks for LiN₃ on Au is ~ 2. The observed differences in the relative intensity of the 399.0 eV peaks and their FWHM's for N₃ on Si(111) and LiN₃ on Au suggest that the 399.0 eV peak has contributions from other species, i.e., the NH_x species, in the present study.

The 397.4 eV peak could be attributed to the atomic N on the surface, since the same peak was observed for Si=N by Bischoff et al. [6]. In another study, the N ls XPS signal was found to be at 397.7 eV [11] after the complete dissociation of the NH bonds in NH₃. On the other hand, the



Fig. 3. N1s XPS of HN₃ on Si(111)- 7×7 at 100 K and the indicated HN₃ dosages (1 L = 10^{-6} Torr s).



Fig. 4. The laser and thermal effects on N Is XPS of 10 L HN₃ dosed Si(111)-7×7: (a) 10 L HN₃ on Si(111), (b) and (c) after exposing to 1×10^{20} and 3×10^{20} photons; (d) and (e) after annealing the post-irradiated sample at 500 and 800 K, respectively.

401.5 eV peak is more difficult to assign. Considering the corresponding HREELS results obtained under essentially the same experimental conditions which showed a peak at 206 meV due to the NN stretching mode of the N₂ adsorbed on Si(111), we tentatively assigned the 401.5 eV peak to the N1s photoelectron emitted from adsorbed N₂ on Si(111). Furthermore, the 401.5 eV peak intensity is less than twice that of the NH_x peak, suggesting a partial desorption of the N₂ species.

Additional irradiation of the sample with the 308 nm laser (with a total of 3×10^{20} photons) caused the desorption and/or the decomposition of the N₂, N₃ and the HN₃ remaining on the surface. The N Is XPS is dominated by a broad peak centered at 398.1 eV due to the mixture of N, NH and NH₂ species on the surface (see Fig.

4, spectrum c). The overall N1s photoelectron intensity was reduced by 40%, indicating further desorption of the N-containing species.

Annealing this laser irradiated sample at 500 K shifted the N1s peak to 397.7 eV and simultaneously narrowed its FWHM from 2.4 to 2.0 eV, because of the partial breaking of the NH bond (see Fig. 4, spectrum d). The peak has thus more contributions from the N and NH species. Upon annealing the surface at 800 K, the FWHM of the N 1s peak was further reduced to 1.5 eV due to the elimination of the higher energy tail from the NH species, while the peak position remained unchanged. At this temperature, the dissociation of the NH bond was essentially complete as indicated by the corresponding HREELS results. Therefore, this narrower 397.7 eV peak is due mainly to the N species with some contribution from the surviving NH species. The XPS results could be slightly different from those of HREELS, due to the additional dissociation of the adsorbates induced by X-ray irradiation.

4. Discussion

4.1. Dosage dependence

An interesting observation in the present study is that the intensity ratio of the 400.3 to 404.1 eV peaks decreased from 2.38 to 2.02 and then to 1.88 when the HN₃ dosage was increased from 1.5 to 5 and then to 10 L, respectively. At the lowest dosage (1.5 L), the N1s XPS signal intensity of N^{II} is lower than 50% of that of N^I + N^{III}; this is likely due to the contribution to the 400.3 eV peak from the NH species. The N1s XPS for NH on Si(111) was reported to be $\sim 398.5 \text{ eV}$ [6,11] which could not be separated from the 400.3 eV peak measured in the present study. This is also supported by the relatively large FWHM of the 400.3 eV peak as compared with the cases of HN₃ condensed on Au [38] and adsorbed on Si(111)-7 \times 7 at higher dosages (Fig. 1). On the other hand, we also speculate that at lower dosages, HN₃ adsorbed on Si(111) through the interaction of the N^{II} atom with a Si dangling bond, because N^{II} is more positively charged

(higher binding energy) and the Si dangling bond is essentially filled with electrons [14]. Such an interaction might cause a distortion of the HN₃ molecule with the N^I and N^{III} atoms pointing towards the vacuum and thus might attenuate the photoelectron signal from the N¹¹ atom. When the HN₃ dosage was increased, Si dangling bonds would be saturated and hydrogen bonding would take place between two HN₃ molecules. The presence of hydrogen bonding, as indicated by the appearance of the strong 60 meV peak in HREELS due to the intermolecular torsional vibration, would cause a redistribution of the electrons in the HN₃ molecules and thus could attenuate the N1s XPS signals from the N^1 and N^{III} atoms, because both of these atoms are involved in hydrogen bonding.

It was also noted that a minor peak at ~ 398.1 eV became stronger with increasing HN₃ dosage. By comparing with earlier XPS studies of NH, species on Si(111), where peaks at 398.8 eV, 398.5 and 397.7 eV for NH₂, NH and atomic N, respectively, were reported [11], the 398.1 eV peak could therefore be attributed to the NH $_{x}$ (x = 0,1) species, resulting from the dissociation of the $HN-N_2$ bond in HN_3 and from further cracking of the NH bond. Furthermore, since the experiments were carried out continuously, i.e., after one XPS measurement, without cleaning the surface, more HN₃ was dosed on the sample for the subsequent XPS recording, we believe that the increase of the 398.1 eV peak intensity at higher dosages is due to the prolonged X-ray irradiation rather than the dosage effect. The X-ray induced dissociation of the adsorbates was also reported by Lee et al. [38] for HN_3 condensed on Au as well as by Kilday et al. [7] and Bu et al. [15] for NH_3 and N_2H_4 on Si(111), respectively. In the present study, the other dissociation product would be the N₂ species, which may or may not desorb from the surface at 100 K. However, by close examination of the spectra, we found that there is obviously some extra signal in the ~ 402 eV region which can be attributed to the N1s photoelectron from N_2 . This signal increased in parallel with that of the 398.1 eV peak and became much more intense after the 308 nm laser irradiation.

4.2. Laser-induced surface reactions

As a 10 L HN₃ dosed Si(111) sample was exposed to 1×10^{20} photons, N₃, N₂ and NH_x (x = 0.1 and 2) adspecies were identified on the surface. In HREELS, a peak at 206 meV was observed, which is attributable to the NN stretching mode for the adsorbed N_2 . When N_2 adsorbed end-on on Ni(110) [31], W(100) [32] and Pt(111) [33], this mode was observed at 265 meV or higher frequencies; however, when it was adsorbed side-on on Fe(111) [30], its frequency was shifted down to 185 meV. The observed 206 meV peak here suggests that N_2 may adsorb side-on on Si(111), but the N-N bond appeared to be weakened to a lesser extent on Si(111) than on Fe(111). The larger red-shift for N_2 on Fe is likely due to the more efficient electron backdonation from the surface to the N_2 molecule. We also compared the N-N stretching mode for N_2 on Si(111) with that for the Si- N_2 molecule isolated in Ar matrices which showed peaks at 60 and 215 meV for the Si-N₂ and N=N stretching modes, respectively [40,41]. This comparison also leads us to conclude that N_2 adsorbed on Si(111) with a side-on rather than an end-on geometry. Other evidence supporting the side-on adsorption of N_2 on Si(111) is that in a corresponding HREEL spectrum taken at 10° off-specular angle (not shown here), the 206 meV peak intensity was only reduced by about three times while that of the elastic peak was reduced by more than 50 times. Such an adsorption geometry for the N_2 on Si(111), similar to that suggested for N_2 on Fe(111) [30], can also be established from the corresponding XPS results.

In XPS measurements, the 401.5 eV peak can be related to the N₂ adspecies. This peak is close to the one which appeared at ~ 399 eV reported for a π -bonded N₂ on Fe(111) [30,42], but it is quite different from those for the N₂ physisorbed end-on on metal surfaces, where two peaks at ~ 406 and ~ 401 eV were observed and attributable to the distal and proximal N atoms, respectively [30,42]. When N₂ bonded end-on on W(110) [43], the N1s XPS for N₂ showed a peak at ~ 400 eV with an FWHM of 3.7 eV. The similar behavior of the N1s XPS for N₂ on Si(111) and Fe(111) again supports that the N_2 adsorbed on Si(111) in a π -bonded side-on geometry, so that the chemical environments of the two N atoms are similar and give a single N1s peak at 401.5 eV. The observed higher binding energy for N_2 on Si(111) than on Fe(111) indicates a more efficient electron back-donation from the latter surface as alluded to above. This conclusion is consistent with that established from the HREELS results. On the other hand, the relatively large FWHM of the peak (1.7 eV) and the fact that the peak cannot be well-fitted by one single Gaussian distribution suggest a nonequivalent electronic charge on the two N atoms. Furthermore, since the 401.5 eV peak intensity is only ~ 92% that of the sum over NH $_x$ (x = 0,1,2) species, we estimate that about 54% N₂ desorbed from the surface under the indicated experimental conditions if all N atoms give equal signal intensity to the N1s photoelectrons. Finally, it should be pointed out that the distance between the Si dangling bonds is rather large (> 5 Å) on Si(111)-7 \times 7, therefore it is unlikely for N₂ to form di- σ bonds with two Si surface atoms.

It is not surprising to have N_2 as one of the photodissociation products, since the HN–NN bond strength is much weaker than those of the H–N₃ and HNN \equiv N bonds and the HN₃ + $h\nu \rightarrow$ NH + N₂ process is the primary reaction channel observed in the gas phase HN₃ photolysis [20–22]. Interestingly, in the present case, some of the N₂ species remained on the surface after the initial laser irradiation, while in a controlled experiment we found no obvious change in HREELS after exposing the Si(111)-7 × 7 surface to 10 L N₂ at 100 K. This observation suggests that one or more N atoms have bonded to Si surface atoms already, before the HN₃ dissociation.

As to the N₃ species, it was clearly evident by the presence of the two peaks at 399.0 and 403.4 eV in the N 1s XPS. These two peaks are identical to those observed for LiN₃ on Au [38]. However, the intensity ratio of the 399.0 to 403.4 eV peaks is higher in the present case, likely due to the contributions to the 399.0 eV peak from other N-containing species, such as NH_x (x = 1,2), in addition to those from the N¹ and N¹¹¹ atoms in the N₃ radical. The N 1s XPS of the NH and NH₂ on Si(111) were reported at 398.5 and 398.8 eV, respectively, which could not be separated from the 399.0 eV peak. If we assume that all N atoms have the same cross section for the N1s photoelectrons as in the case of LiN_3 on Au, the contribution from NH_x species to the 399 eV peak would be about 20%.

The presence of N_3 and NH_x species were also indicated in the corresponding HREELS spectra. The N_3 species showed two peaks at 178 and 255 meV, which compare favorably with those of 167–171 and 253–264 meV reported in IR for azide ions [34–36]. The fair agreement between HREELS results for N_3 on Si(111) and IR results for azide ions and the good agreement between N 1s XPS results for N_3 on Si(111) and LiN₃ on Au imply that charge donation from the Si surface to the N_3 radical occurs to some extent.

The NH_{y} species showed peaks at 421 meV due to the NH stretching vibration of either NH or NH_2 species on the Si substrate. Such a peak was observed earlier in the studies of NH₃ on Si(111) [10] after the partial cracking of the NH bonds and N_2H_4 on Si(111) after the partial breaking of the NH and NN bonds [15]. In all cases, the 421 meV peak was attributed to the NH_{r} (x = 1,2) species. The presence of the NH_{2} was also indicated by the shoulder at 187 meV due to the NH₂ deformation vibration, which is consistent with the value of 192 meV reported by Chen et al. for NH_2 on Si(111) [10]. Other supporting evidence for the formation of NH_x (x = (0,1,2) species is the appearance of the new peak at 113 meV, which has contributions from the SiNH, stretching, Si₂NH bending and SiNH, rocking vibrations. The 113 meV peak may also have the contribution from the Si₃N species, because it showed peaks at 115 and 93 meV due to the asymmetric stretching and the symmetric deformation modes, respectively [12].

4.3. Comparison with gaseous HN_3 photolysis

Laser-induced dissociation of gaseous HN₃ has been studied extensively [20–22]. N₂ and NH(¹ Δ) have been shown to be the dominant decomposition products. When excited at 266 nm, > 99.8% of the products were identified to be N₂ + NH(¹ Δ) [20]. The latter species was measured to be vibrationally cold with a rotational temperature of about 1200 K [20]. Similarly, UV photolysis of HN₃ at 193 and 248 nm produced the same products with differing internal excitations [21]. Furthermore, although HN₃ absorbs the 308 nm wavelength light, the photon energy is barely sufficient to break the NH bond [22] in the gas phase. However, we found that the yields of N₃ and N₂ + NH are comparable, when the 10 L HN₃ adsorbed on Si(111) was irradiated with 1×10^{20} photons at 308 nm. Such an obvious difference in the behavior of HN₃ in the gas phase and the adsorbed state on Si(111)-7 × 7 may be attributed to the following:

(a) When adsorbed on Si(111), the energy required to break the NH bond in HN_3 is reduced to such an extent that the 308 nm photon energy will suffice. This is not surprising, since partial NH bond-breaking was noted in both NH_3 and N_2H_4 adsorbed on Si(111) at ~ 100 K without laser irradiation. In the case of HN_3 on Si(111) at 100 K, such a bond-breaking process could not be clearly ascertained, because the vibrational frequency of the indicative Si-H product stretching mode overlaps with that of the HNN=N stretching mode. Although our XPS analysis suggested a slight dissociation of the HN_3 upon adsorption, the dissociation could be induced by the X-ray irradiation as alluded to above.

(b) The secondary reaction, $NH(^{1}\Delta) + HN_{3} \rightarrow$ $NH_2 + N_3$, may take place on the surface. It is known that the radiative decay of the excited $NH(^{1}\Delta)$ species is very slow in the gas phase [20], although its lifetime may be shortened when it is adsorbed on the surface. However, under the experimental conditions employed in the present study with the relatively high dosage (10 L), the fast relaxation process of the NH($^{1}\Delta$) species through the direct coupling to the surface might not be possible due to the presence of overlayer adsorbates. In addition, the relative concentrations of the NH($^{1}\Delta$) and HN₃ on the surface could be much higher than those in the gas phase studies. Furthermore, the rate of the NH($^{1}\Delta$) + HN_3 reaction is relatively fast, $k_r = 9.3 \times 10^{-11}$ $cm^3/mol \cdot s$ [22], such a secondary reaction is likely to occur within the layers. This may be



Fig. 5. The 308 nm laser effect on HREELS of 0.3 L HN₃ dosed Si(111)- 7×7 at 100 K.

supported by the appearance of the NH₂ species which could be identified in the HREELS and was also confirmed by the corresponding XPS results. However, we cannot rule out the possibility that NH₂ may also be produced by other surface reactions as reported in photodissociation of HN₃ in gas phase [20–24], e.g., H + HN₃ \rightarrow NH₂ + N₂.

Whether or not the secondary reactions occur on the surface could be verified by the experiments carried out under the submonolayer dosage conditions. As shown in Fig. 5, the HREELS results taken from a 0.3 L HN₃ dosed sample were different from those obtained at higher dosages. After the 0.3 L HN₃ dosed Si(111) was irradiated with 1×10^{20} photons, the molecular vibrational features weakened but clearly still existed. This is likely because of the fast relaxation of the excited adsorbates through the direct coupling, e.g., dipole interaction, between the surface and the adsorbates under the lower dosage conditions. In addition, the lower adsorbate concentrations would reduce the possibility of secondary reactions, which is indicated by the absence of any obvious N₃ and NH₂ features in HREELS as observed in the case of the 10 L HN_3 dosed sample. On the other hand, the shift of the NH deformation mode from 143 to 137 meV, the NH stretching mode from 414 to 418 meV, and the HN₃ asymmetric deformation mode at 90 to 100 meV due to a partial contribution from the SiN stretching mode suggest some dissociation of the HN₃ molecules into NH and N₂ species. There was no strong peak at 206 meV which is expected for the N₂ stretching mode in SiN_2 . This is probably due to the desorption and lower concentration of the N2 species under lower dosage conditions. Additional laser irradiation caused a further dissociation of the adsorbed HN₃ species. The 157 meV peak due to the HN₃ symmetric stretching mode vanished, and the 100 and 418 meV peaks shifted further to 105 and 421 meV, respectively, because of the formation of SiNH_x (x = 0,1) species. The 105 meV peak should also have some contribution from the NH rocking vibration, since the corresponding NH stretching mode is still strong. The remaining intensity of the 265 meV peak, which is now shifted to 260 meV, is mainly due to the Si-H stretching mode, although it may still contain some contribution from the asymmetric stretching mode of the survived HN₃ species. The Si-H species should also be formed after the initial laser irradiation $(1 \times 10^{20} \text{ photons})$, which would explain the apparent lower attenuation of the 265 meV peak intensity as compared with that of the 157 meV peak.

5. Conclusion

The 308 nm laser-induced photodissociation of HN_3 on Si(111)-7 × 7 at 100 K was studied with HREELS and XPS. The results obtained under high dosage conditions indicated that surface species such as NH_x (x = 0,1,2), N_2 and N_3 were present with comparable concentrations.

These species may be formed in the upper adlayers by the mechanism akin to that occurring in the gas phase [20–24]:

$$\begin{aligned} HN_3(a) + h\nu &\rightarrow NH(^1\Delta)(a) + N_2(a), \\ NH(^1\Delta)(a) + HN_3(a) &\rightarrow NH_2(a) + N_3(a) \end{aligned}$$

Continued irradiation with the laser caused the partial desorption and the dissociation of these surface species, including the small amount of surviving HN_3 , while the NH_x species remained on the surface. The secondary reaction involving $NH(^1\Delta)$ given above, however, occurred to a far lesser extent under submonolayer adsorption conditions, possibly because of the efficient relaxation of the excited NH by the surface: $NH(^1\Delta)(a) \rightarrow NH(^3\Sigma^-)(a)$.

The high efficiency in producing the reactive NH_x species on silicon surfaces by the UV laser irradiation of adsorbed HN_3 suggests that it may be possible to employ the laser chemical vapor deposition technique for silicon and group-III nitride film preparations. This possibility has indeed been successfully tested recently for the deposition of InN films with good surface morphology at relatively low temperatures (300–700 K) [44]. It should also be mentioned that similar experiments were carried out for the photodissociation of HN_3 on Si(100)-2 × 1 with essentially the same results.

Acknowledgement

The authors gratefully acknowledge the support of this work by the Office of Naval Research.

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