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The 308-nm laser photodissociation of HN_3 adsorbed on $\text{Si}(111)-7\times 7$

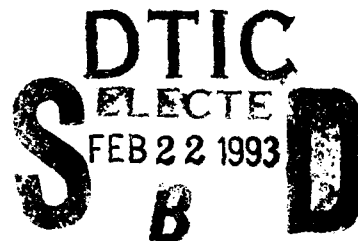
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Abstract

The photodissociation of HN_3 adsorbed on $\text{Si}(111)\text{-}7\times 7$ was investigated at 308 nm 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 of a 10 L HN_3 dosed $\text{Si}(111)$ surface with 1×10^{20} photons. The N_3 species showed two stretching modes at 178 and 255 meV, while that of the N_2 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 HN_3 for laser-induced chemical vapor deposition of Si_3N_4 and group-III nitrides at low temperatures is suggested.

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1. Introduction

The thermal decomposition of N-containing species, such as NH_3 , N_2H_4 and HN_3 etc. on Si substrates has been studied extensively [1-19] using different surface sensitive techniques including HREELS, UPS, XPS, AES, LEED and STM. On both Si(111)-7x7 and Si(100)-2x1 surfaces, NH_3 was found to dissociatively adsorb on the substrates at $T \cong 80$ K. Further thermal treatment caused continuous NH bond breaking, although the NH_2 species behaved differently on the two surfaces [10]. Above 800 K, the dissociation of NH_x species and the desorption of H_2 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 N_2H_4 on Si(111)-7x7 at 120 K [16]. In this case, the N-N bond started to break at above 600 K. Similar results were also found for $\text{HN}_3(\text{DN}_3)$ on Si substrates; however, the HN-NN bond breaking occurred at lower surface temperatures [15,17-19].

On the other hand, very few studies on the photodissociation of these N-hydrides on Si surfaces have been reported, although numerous studies on their photodecomposition reactions in the gas phase have been made [20-24]. Surface photolysis is a rather 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, surface heating occurs 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 photogenerated hot carriers from the substrate. In this paper, we report a nonthermal photodissociation of HN_3 adsorbed on Si(111)-7x7 at 100 K under the irradiation of a 308-nm excimer laser. In contrast to the results of the thermal

decomposition of HN_3 on $\text{Si}(111)\text{-}7\times 7$ [18], both N_2 and N_3 were identified in addition to the more stable NH_x species after the irradiation of a 10 L HN_3 dosed sample with 1×10^{20} photons. These results are also different from those of gaseous HN_3 photolysis [20-24], which produces exclusively N_2 and $\text{NH} (^1\Delta)$ in the UV region.

2. Experimental

The experiment was carried out in a custom-designed UHV system with a base pressure of $<1 \times 10^{-10}$ torr as described elsewhere [16-19]. Both the $\text{Si}(111)$ surface and the HN_3 sample were prepared in the same manner as described in ref. [18]. An Mg X-ray source was used for the XPS measurements with a pass energy setting at 50 eV to give a resolution better than 1.3 eV (FWHM), the value obtained for the N_{1s} XPS taken from a well prepared Si_3N_4 sample. In the HREELS (High-Resolution Electron Energy Loss Spectroscopy) measurements, an electron beam with a primary energy of 5 eV and FWHM (Full Width at Half Maximum) 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 typical laser fluence is about $20 \text{ mJ}(3 \times 10^{16} \text{ photons})/\text{cm}^2$. pulse on the surface.

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 HREERLS

When 10 L HN_3 was dosed on $\text{Si}(111)\text{-}7\times 7$ at 100 K, HREELS produced peaks at 60, 150, 266 and 388 meV as shown in Fig. 1. As discussed earlier in ref. [18], these peaks are due to the monomeric, dimeric and/or polymeric HN_3 adsorbed on surface. The 150 meV peak is actually 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 HN_3 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 NH_3 dosage was increased.

When the 10 L HN_3 dosed $\text{Si}(111)$ was exposed to a 308 nm excimer laser irradiation, the following changes were noted, indicating the formation of NH_x ($x = 0, 1, 2$), N_2 and N_3 species on the surface. The NH species were clearly indicated by the broadening and the blue-shifting of the 388 meV peak, which has now a considerable contribution from the 421 meV component. Such a peak was observed earlier in the studies of NH_3 and N_2H_4 on $\text{Si}(111)$ after the partial breaking of NH and NN bonds; the peak was attributed to the NH_x ($x = 1, 2$) species. The presence of the NH_2 was also indicated by the shoulder at 187 meV owing to the NH_2 deformation vibration, which became a distinct peak as the sample was further irradiated with the laser. The

N_2 species, on the other hand, was 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]. When N_2 adsorbed "end-on" on Ni(110) [31], W(100) [32] and Pt(111) [33], this mode was observed to be 265 meV or higher frequencies, while it was adsorbed "side-on" on Fe(111) [30], its vibrational frequency was shifted down to 185 meV. The observed 206 meV peak here, thus suggests a "side-on" adsorption of N_2 on Si(111). However, the N-N bond, appeared to be weakened to a lesser extent on Si(111) than on Fe(111). This smaller red-shift of the NN stretching mode for N_2 on Si(111) is likely because of the more efficient electron back-donation from Fe(111) to the N_2 molecule. We can also compare 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- N_2 and N=N stretching modes, respectively [34-35]. Such a comparison again 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 3 times while that of the elastic peak was reduced by more than 50 times. It should be pointed out that the N_2 adsorbed "side-on" does not necessarily mean that the N=N bond is exactly parallel to the surface plane, because the reconstructed Si(111)- 7×7 surface has a relatively open and complicated structure. For example, Si adatoms and rest-atoms are back-bonded to the three other Si atoms underneath them and each rest-atom is surrounded by three adatoms above it, this nearly three-fold symmetric environment may cause a slight tilting of the adsorbed N_2 . Such an adsorption geometry for the N_2 on Si(111) can also be established from the corresponding XPS results as will be discussed later. A similar adoption geometry was suggested for N_2 on Fe(111) [30].

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- N_3 and HNN $\equiv$ N bonds and the $HN_3 + h\nu \rightarrow NH + N_2$ process is the primary reaction channel observed in the gas phase HN_3 photolysis [20-22]. Interestingly, in the present case, some of the N_2 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)-7x7 surface to 10 L N_2 at 100 K. This observation suggests that before HN_3 dissociation, one or more N atoms have bonded to Si surface atom already.

As to the N_3 species, it could be related to the shift of the 150 and 266 meV peaks of the HN_3 to 178 and 255 meV, respectively, because peaks at 167-171 and 253-264 meV were observed in IR for azide ions [36-38]. The blue shift of the N-NN and the red-shift of the NN $\equiv$ N stretching modes should be expected, because electrons in π bonds delocalize across the whole N_3 radical after the dissociation of the NH bond. The N_3 formation was further confirmed in our XPS results as will be discussed shortly. Finally, the remaining peak at 390 meV indicates that a small amount of HN_3 molecules survived on the surface.

Further laser irradiation caused additional dissociation and also induced a partial desorption of the N_2 , N_3 , and HN_3 species produced. Resonance peaks at 178, 206 and 255 meV essentially disappeared, while the NH stretching mode was narrowed and shifted to 422 meV, and a new peak at 187 meV due to the NH_2 deformation mode was fully developed (see Fig. 1). 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_x stretching, NH_2 rocking and Si_2NH bending vibrations [12], was also greatly enhanced

by further laser irradiation. This HREEL spectrum is clearly dominated by the NH_x ($x = 0, 1, 2$) 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 by essential disappearance of the 140 and 187 meV, modes due to the NH bending and NH_2 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.

3.2 XPS

Fig. 2 shows the N_{1s} XPS of HN_3 on Si(111)-7x7 at 100 K with the indicated dosages. The N_{1s} signal is mainly composed of two peaks at 404.1 and 400.3 eV, originated from N^{II} and N^{I} plus N^{III} atoms, respectively; where the superscripts denote the nitrogen atoms at different positions in the HN_3 molecule; $\text{HN}^{\text{I}}\text{N}^{\text{II}}\text{N}^{\text{III}}$. We have discussed previously in ref. [18] that the broader and more intense peak at 400.3 eV could be deconvoluted into two peaks located at 400.8 and 399.8 eV with equal intensities and same FWHM's as illustrated in the figure. These two peaks, derived from the N^{III} and N^{I} 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 [39] and with those from an atomic charge calculation [40].

Interestingly, the intensity ratio of the 400.3 to 404.1 eV peaks decreased from 2.38 to 2.02 and then to 1.88 as the HN_3 dosage was increased from 1.5 to 5 and then to 10 L, respectively. At the lowest dosage (1.5 L), the N_{1s} XPS signal intensity of N^{II} is smaller than 1/2 that of N^{I} plus N^{III} ; this is likely due to the contribution from NH species to the 400.3 eV peak. The N_{1s} XPS for NH on Si(111) was reported to be

~398.5 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 larger FWHM of the 400.3 eV peak as compared with the cases of HN_3 condensed on Au [39] and adsorbed on Si(111)-7x7 at higher dosages. On the other hand, we also speculate that at lower dosages, HN_3 adsorbed on Si(111) through the interaction of 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 HN_3 molecule with the N^{I} and N^{III} atoms pointing towards the vacuum and thus attenuate the photoelectron signal from the N^{II} atom. As the HN_3 dosage was increased, Si dangling bonds would be saturated and hydrogen bonding may take place between two HN_3 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 certainly cause a redistribution of the electrons in the HN_3 molecules and thus could attenuate the N_{1s} XPS signals from the N^{I} 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 HN_3 dosage. By comparing with earlier XPS studies of NH_x species on Si(111), where peaks at 398.8 eV (398.6), 398.5 (398.0) and 397.7 (397.0) eV for NH_2 , NH and atomic N, respectively, were reported [6,11]. The 398.1 eV peak could 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 HN_3 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. for HN_3

condensed on Au as well as by Kilday et al. [7] and Bu et al. [16] for NH_3 and N_2H_4 on Si(111), respectively. In the present study of HN_3 on Si(111), the other dissociation product would be the N_2 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 N_{1s} 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 as will be discussed below.

Fig. 3 illustrates the effects of laser irradiation and thermal heating after the irradiation on the N_{1s} XPS signal of HN_3 on Si(111). As discussed above, prior to laser irradiation, the N_{1s} XPS peak could be deconvoluted into at least 4 peaks derived from the HN_3 (3 peaks) and the NH_x species. When the 10 L HN_3 dosed sample was irradiated with 1×10^{20} photons at 308 nm, 4 major peaks at 399.0, 401.5, 403.4 and 397.4 eV were present in the XP spectrum.

The 399.0 and 403.4 eV peaks are identical to those of the XPS results taken from LiN_3 condensed on an Au surface [39]. The 403.4 peaks also have essentially the same FWHM's in both cases. However, the 399.0 eV peak is broader for N_3 on Si (FWHM = 1.92 eV) than that for LiN_3 on Au (~ 1.4 eV). Furthermore, the intensity of the 399.0 eV peak is more than 2 times that of the 403.4 eV peak for HN_3 on Si(111) after 308-nm laser irradiation, while the intensity ratio of these two peaks for LiN_3 on Au is ~ 2 . These observations indicate that there are some 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 N^{I} and N^{III} atoms in the N_3 radical. The N_{1s} XPS of the NH and NH_2 on Si(111) were reported at 398.5 and 398.8 eV, respectively, which would not be separated from the 399.0 eV peak. If we assume that all N atoms have the same cross-section for the N_{1s} 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%. It is worth mentioning that the good agreement between N_{1s} XPS results for N_3 on Si(111) and LiN_3 on Au as well as the fair agreement of the HREELS result for N_3 on Si(111) with that obtained from an IR absorption measurement for azide ions implies a charge donation from Si(111) to the N_3 radical to some extent.

The 397.4 eV peak could be attributed to the atomic N on the surface, since the same peak was observed for $Si \equiv N$ by Bischoff et al. [6]. In another study, the N_{1s} XPS signal was found to be at 397.7 eV [11] after the complete dissociation of the NH bond in NH_3 . On the other hand, the 401.5 eV peak is somewhat 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 N_2 adsorbed on Si(111), we tentatively assigned the 401.5 eV peak to the N_{1s} photoelectron emitted from adsorbed N_2 on Si(111). This is similar to the peak which appeared at ~399 eV previously reported for a π -bonded N_2 on Fe(111) [30]. This peak is quite different from those for "end-on" physisorbed N_2 on metal surfaces, where two peaks at ~406 and ~401 eV were observed and attributed to the up and down N atoms, respectively [30]. In the π -bonded state, N_2 chemisorbed on Fe(111) with both N atoms interacting with the surface and the NN stretching vibrational frequency was down-shifted to 185 meV. While for the N_2 on Si(111), the NN stretching mode appeared at 206 meV. This smaller red shift of the NN stretching mode is probably due to a lesser extent of electron back-donation from Si than Fe to N_2 ; this could at least partially account for the observed higher N_{1s} bonding energy for N_2 on Si than on Fe(111). The similar behavior of the N_2 on Si(111) and Fe(111) coupled with the fact that there is no obvious peak at ~406 eV in the present N_{1s} XP spectrum, suggests that the N_2 adsorbed on Si(111) also has a π -bonded "side-on" geometry, so that the chemical environments of the two N atoms are similar and give a

single N_{1s} peak at 401.5 eV. On the other hand, the relatively large FWHM of the peak (1.7 eV) and the fact that the peak cannot be well-fitted with one single Gaussian distribution suggest a nonequivalent electronic charge on the two N atoms. It should be pointed out that the distance between the Si dangling bonds is rather large ($>5\text{\AA}$) on Si(111)- 7×7 , therefore it is unlikely for N_2 to form di- σ bonds with two Si surface 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 estimated that about 54% N_2 desorbed from the surface under the indicated experimental conditions if all N atoms give equal signal intensity to the N_{1s} photoelectrons.

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 N_2 , N_3 and the HN_3 remained on the surface. The N_{1s} XP spectrum is dominated by a broad peak centered at 398.1 eV due to the mixture of N, NH and NH_2 species on the surface (see Fig. 3). The overall N_{1s} photoelectron intensity was reduced by 40%, indicating a further desorption of the N-containing species.

Annealing this laser irradiated sample at 500 K shifted the N_{1s} 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. 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. It is worth mentioning that the XPS results could be slightly different from those of HREELS, owing to the additional dissociation of the adsorbates induced by the X-ray irradiation.

4. Discussion

Laser-induced dissociation of gaseous HN_3 has been studied fairly extensively. [20-22] N_2 and $\text{NH}(^1\Delta)$ have been shown to be the prominent decomposition products. When excited at 266 nm, >99.8% of the products were identified to be N_2 + $\text{NH}(^1\Delta)$ [20]. The latter species was measured to be vibrationally cold with a rotational temperature of about 1200 K [20]. Similarly, the UV photolysis of HN_3 at 193 and 248 nm produced the same products with differing internal excitations [21]. Furthermore, although HN_3 adsorbs the 308 nm wavelength light, the photon energy is barely enough to break the NH bond [22] in the gas phase. However, in the present study, we found that the yields of N_3 and N_2 + NH are comparable, when the 10 L HN_3 adsorbed on Si(111) was irradiated with 1×10^{20} photons at 308 nm. Such an obvious difference in the behavior of HN_3 in the gas phase and the adsorbed state on Si(111)-7x7 may be attributed to the following reasons:

1. 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 bond-breaking process would not be clearly ascertained, because the vibrational frequency of the indicative Si-H product stretching mode overlaps with that of the $\text{HNN} \equiv \text{N}$ 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 before.

2. The secondary reaction $\text{NH}(^1\Delta) + \text{HN}_3 \rightarrow \text{NH}_2 + \text{N}_3$, may also take place on the surface. It is known that the radiative decay of the excited $\text{NH}(^1\Delta)$ 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 relaxing process of the $\text{NH}(^1\Delta)$ 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 $\text{NH}(^1\Delta)$ and HN_3 on the surface could be much higher than those in the gas phase studies. Furthermore, the rate of the $\text{NH}(^1\Delta) + \text{HN}_3$ reaction is relatively fast, $k_r = 9.3 \times 10^{-11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ [22], such a secondary reaction is likely to occur within the layers. This may be supported by the appearance of the NH_2 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 NH_2 may also be produced by other surface reactions, such as $\text{H(a)} + \text{NH(a)} \rightarrow \text{NH}_2\text{(a)}$.

5. Conclusion

The (308 nm) laser-induced photodissociation of HN_3 on $\text{Si}(111)\text{-}7\times 7$ at 100 K was studied with HREELS and XPS. After an initial laser irradiation with 1×10^{20} photons, surface species such as NH_x ($x = 0, 1, 2$), N_2 and N_3 were identified with comparable concentrations. 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 results are different from those of the gas phase HN_3 photo-dissociation, in which the $\text{HN}_3 + h\nu \rightarrow \text{H}_2 + \text{NH}(^1\Delta)$ reaction has been shown to be the dominant process (>99%). The high efficiency in producing the reactive NH_x species on silicon surfaces by UV laser irradiation suggests that it may be possible to employ the LCVD (laser chemical vapor

deposition) technique for silicon and group-III nitride film preparations. It should be mentioned that similar experiments were carried out for the photodissociation of HN_3 on $\text{Si}(100)\text{-}2\times 1$ with essentially the same results.

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Figure Captions:

Fig. 1 a) The laser effect on HREELS of 10 L HN_3 dosed Si(111)-7x7 at 100 K and
b) the thermal effect on HREELS of HN_3 on Si(111) after being exposed to 3×10^{20} photons.

Fig. 2 N_{1s} XPS of HN_3 on Si(111)-7x7 at 100 K and the indicated HN_3 dosages ($\text{IL} = 10^{-6} \text{ torr}\cdot\text{s}$).

Fig. 3 The laser and thermal effects on N_{1s} XPS of 10 L HN_3 dosed Si(111)-7x7:
a) 10 L HN_3 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.

