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NH_3 on Si(111)7×7: Dissociation and surface reactions

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Core-level and valence-band photoelectron spectroscopy on the dissociative adsorption of ammonia on Si(111)7×7 is presented. Adsorption at room temperature produces three nitrogen 1*s* components, of which two are assigned to NH_2 and one to NH, with an initial tendency for double dissociation. These doubly dissociated species can be connected to the development of silicon atoms coordinated with two nitrogen atoms, necessitating silicon-silicon bonds to be broken. The dominating picture evolving is thus adatoms saturated by NH_2 with a NH group inserted into one backbond, and hydrogen preferentially capping restatoms. The dissociation proces is hence much more complex than generally proposed before. This is further accentuated by the fact that not all adatoms appear reacted. When annealed above 600 K the dissociation process progresses and atomic nitrogen appears at 700 K, to be the only remaining specie at 850 K. At 1200 K, further changes in the N 1*s* core level indicates true silicon nitride formation. [S0163-1829(98)04404-X]

INTRODUCTION

The silicon-ammonia system has received much attention over the years. The general motivation has been the interest in silicon nitride, where ammonia has been the most frequently used nitrogen source in chemical vapor deposition (CVD) growth.[1] Silicon nitride is an insulator with wide applicability in microelectronics as passivator and diffusion barrier at surfaces and interfaces.[2,3] Although silicon nitride is usually grown under quite different conditions compared to the more simplified studies performed, an improved general understanding of the silicon-ammonia reaction system can hopefully contribute to advances also in synthesis. In this context, the complex Si(111)7×7 reconstruction, which displays a variety of surface sites, provides the opportunity to study the effect of local electronic structure on surface reactions, and the subsequent electronic structure modification. The response of the surface to impinging ammonia molecules is thus also a test of the understanding of the 7×7 reconstruction.

The Si(111)7×7 reconstructed surface is perhaps the most studied of all semiconductor surfaces. The commonly accepted surface model is the so called dimer adatom stackingfault (DAS) model, by Takayanagi *et al.*[4] This model reduces the number of dangling bonds (DB's) within the surface unit cell from 49 to 19, of which 12 are associated with adatoms, 6 with restatoms, and one with the corner hole. There has been some controversy regarding the assignment of the silicon rest and adatom surface components in core-level photoelectron spectroscopy (PES). Most of the studies published favors an initial state derived model where charge transfer from adatoms to restatoms[5,6] increases the core-level screening at the restatom, with a lower binding energy as a result, and vice versa for the adatoms.[7–9] However, the reverse restatom/adatom assignment have been proposed.[10] In this work the initial state model is applied with good consistency.

A number of studies using various surface sensitive techniques have been performed on the adsorption of ammonia on Si(100) and Si(111).[11–27] The main disagreement in previous studies on the (111)7×7 reconstructed surface connects to whether the dissociative adsorption of ammonia displays all the possible dissociation fragments, i.e., NH_2, NH, and N, where the controversy concern the NH radical. There has been an inclination for a simple adsorption model where the restatom and adatom DB's of the 7×7 surface all are passivated by NH_2 and H, respectively.

In this paper the modification of the silicon 7×7 surface electronic structure due to chemisorbed ammonia species is examined by means of surface core-level and valence-band (VB) PES. The reacted surface exhibit all ammonia derived species, i.e., NH_2, NH, and N. The first two after room temperature (RT) exposure and atomic nitrogen when annealed to 700 K. Clear evidence of broken silicon bonds are found as is expected with NH radicals present. VB data also indicates that the surface passivation is incomplete. The RT dissociation process must hence be interpreted using a much more complex model than previously proposed. At 850 K all hydrogen has left the surface, and nitrogen is the only residual ammonia specie. Further annealing to 1200 K indicates a partial reformation of the nitrogen atoms which is interpreted as the formation of small silicon nitride networks.

EXPERIMENTAL

The photoemission experiments were performed at beam line 22 at The National Synchrotron Radiation Facility MAX-LAB (Lund, Sweden) using a modified SX-700 plane-grating monochromator and a 200 mm radius hemispherical analyzer of Scienta type,[28] allowing an angular acceptance of 16° in the present setup. A preparation chamber in connection with the photoemission chamber contained gas inlet system, resistive sample heating and low-energy electron diffraction (LEED) optics for initial surface studies. The base pressure in the photoemission and preparation chambers was 1×10^{-10} Torr or better. Sharp 7×7 LEED patterns were achieved after heating the pre-etched[29] samples (*p* doped) to 950 °C, during which the pressure never exceeded 5×10^{-10} Torr. Cleanliness of the surface was monitored with

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photoemission through the 7×7 surface VB characteristics and the absence of O 1s and C 1s core-levels. Exposure of the 7×7 surfaces to ammonia were done at pressures in the 10^{-9}–10^{-8} Torr range and are measured in Langmuir $(1\,L = 1\times10^{-6}\ \text{Torr}\times\text{sec})$. Annealing steps of 50 K, with a duration of 60 sec, were monitored with a pyrometer. The overall energy resolution used was approximately 100 meV for the Si 2p level, 200 meV for the VB, and 500 meV for the N 1s level, as derived from the Fermi edge of a platinum foil in electrical contact with the sample.

The N 1s core-level photoemission data was fitted by a nonlinear least squares fitting procedure, using Voigt functions.[30] The energy and amplitude of the peaks were always free parameters of the fit while different Gaussian and Lorentzian widths were set manually. N 1s photoemission spectra backgrounds were modelled with exponential functions. All spectra are corrected in energy (platinum foil) and the intensities are normalized to the average background on the low binding energy side (core levels). To improve the reliability of the fitting procedure spectra were recorded with different photon energies. The silicon 2p spectra shown here were all detected at 60° of normal to enhance the surface sensitivity whereas nitrogen 1s and valence-band data were recorded at normal emission.

RESULTS AND DISCUSSION

N 1s. Figure 1(a) shows the nitrogen 1s core-level for increasing ammonia exposures at RT. At small doses, 0.15 L two peaks, separated into A_2 and A_3, are clearly visible in the spectrum. Initially the A_3 peak dominates, but as the dose is increased, the situation reverses. At the same time a third component, denoted A_1, appears. This is not equally clear from the total nitrogen signal, but as the exposure is increased a broadening of the core-level towards higher binding energy is observed. At high coverages (1 and 5 L) this component is essential if good agreement between deconvolution and experimental data is to be accomplished. The difference between the 1 and 5 L spectra is very small, suggesting that the surface is more or less saturated.

Figure 1(b) shows the 5 L RT deposited nitrogen 1s spectra after annealing. Above 600 K the core-level start to change. A new component on the low binding energy side develop whereas the existing components gradually diminishes, starting with the highest binding energy component A_1. At 700 K A_1 is completely gone while A_4 appears, and at 750 K traces of A_2 can no longer be found. At 850 K the N 1s spectrum consists of component A_4 alone.

While the variation in binding energy of the N 1s components at RT, Fig. 1(a), is relatively small (~50 meV), the variation after annealing is larger, with a gradual shift towards higher binding energies of components A_3 and A_4. In fact the Gaussian width of the nitrogen components are increased from the RT value 0.75 eV, up to 1 eV for the single component spectrum at 850 K. A reliable multicomponent fitting of this spectrum could not be accomplished which is necessary if the smaller widths are to be used. This is not necessarily a failure of the fitting procedure. If parts of the existing ammonia species with increasing temperature start to occupy new sites, resulting in a more complex chemisorption state, a broadening of the components seems reasonable.

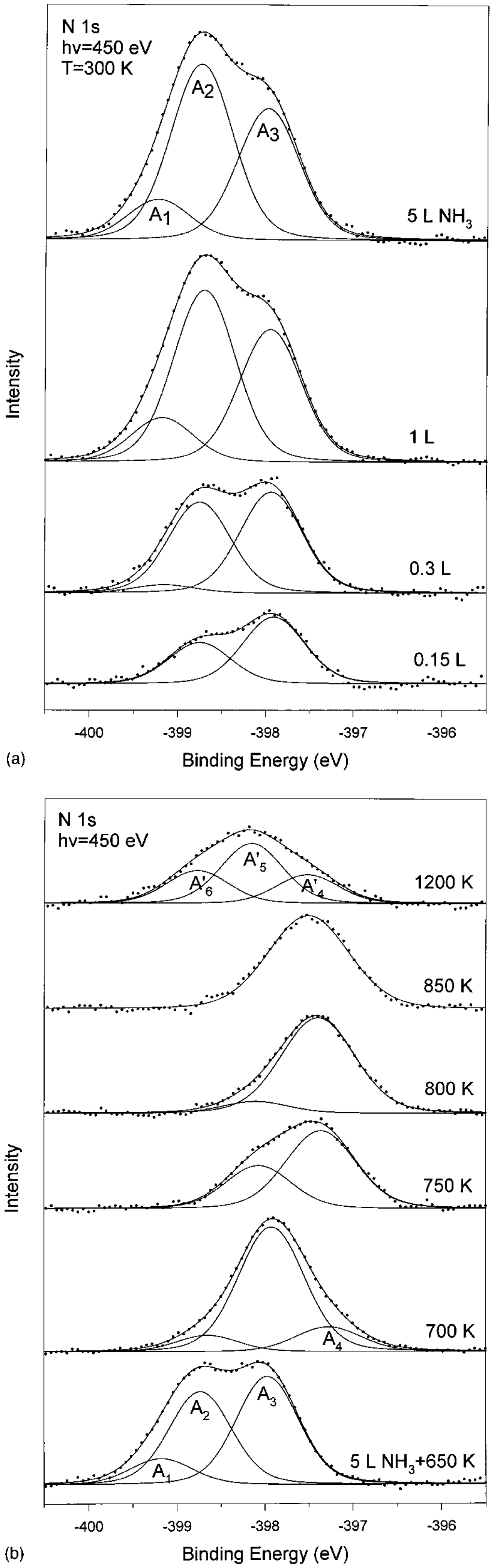

FIG. 1. (a) Nitrogen 1s core-level spectra for increasing ammonia exposures at RT. The total signal is separated into three components: A_1, A_2, and A_3. (b) After annealing of the 5 L dosed surface the dissociation continues, a fourth component A_4 appears at 700 K.

TABLE I. Fitting parameters for the N 1s core level.

Spectrum	Component	Energy (eV)	Intensity (%)	W_G (eV)	W_L (eV)
RT 0.15 L	A_2	398.75	38	0.75	0.15
	A_3	397.92	62	0.75	0.15
RT 0.3 L	A_1	399.16	5	0.75	0.15
	A_2	398.75	45	0.75	0.15
	A_3	397.94	50	0.75	0.15
RT 1 L	A_1	399.18	13	0.75	0.15
	A_2	398.71	49	0.75	0.15
	A_3	397.95	38	0.75	0.15
RT 5 L	A_1	399.22	12	0.75	0.15
	A_2	398.74	50	0.75	0.15
	A_3	397.98	38	0.75	0.15
650 K	A_1	399.16	11	0.75	0.15
	A_2	398.72	41	0.75	0.15
	A_3	397.95	48	0.75	0.15
700 K	A_2	398.67	9	0.75	0.15
	A_3	397.93	76	0.80	0.15
	A_4	397.28	15	0.80	0.15
750 K	A_3	398.06	34	0.80	0.15
	A_4	397.36	66	0.80	0.15
800 K	A_3	398.10	10	0.80	0.15
	A_4	397.40	90	0.90	0.15
850 K	A_4	397.50	100	1.0	0.15
1200 K	A_4'	397.52	24	0.75	0.15
	A_5'	398.16	49	0.75	0.15
	A_6'	398.77	27	0.75	0.15

Furthermore, since the energy resolution is no better than 500 meV, the fitting procedure can only reproduce the main features of the core-level spectrum. All curve fitting parameters and binding energies of the N 1s components are summarized in Table I. At 1200 K intensity is shifted back to higher binding energies, as has been observed before.[18] The spectrum is tentatively (although very well) fitted with the three components A_4', A_5' and A_6'.

With increasing annealing temperature the number of nitrogen components decreases. At 850 K the nitrogen 1s spectrum consists of only the A_4 component. A rational assumption is that this single component corresponds to fully dissociated ammonia, i.e., atomic N triply coordinated to silicon atoms, on or just below the surface. Indeed, previous temperature programmed desorption (TPD)[17,26] and Fourier transform infrared (FTIR)[22] experiments show that little or no hydrogen is left at 850 K. The binding energy of the A_4 peak is 397.40 ± 0.1 eV, which is also in good agreement with what have been measured before for fully dissociated NH_3 (Refs. 12, 21, and 27) on silicon. Further assignments of the core-level components follow an initial state binding energy picture. As H is more electronegative than Si,[31] substituting a N-H bond with a N-Si bond would decrease the core-level binding energy of the nitrogen component. Accordingly the A_3 and A_2 components are assigned to NH and NH_2 radicals, respectively. This confirms the proposed presence of NH on the surface made by Bischoff *et al.*[21] in a previous core-level PES study, as the components here are visually resolved. Colaianni, Chen, and Yates, Jr.[26] reported in an extensive high resolution electron energy loss spectroscopy (HREELS) study, covering temperatures from 80 up to 900 K, evidence for all the ammonia derived radicals on the surface according to $NH_2\leqslant650$ K, 200 K$\leqslant$NH$\leqslant$750 K, and N$\geqslant$700 K, thus in excellent agreement with our results. If the electronegativity discussion above is extended to include component A_1, it suggests that molecular ammonia is present at the RT exposed surface. However, only at lower temperatures, well below 200 K,[26] have molecular NH_3 been observed to be stable on Si(111)7×7. Furthermore, the binding energy of the NH_3 associated core-level peak have been experimentally determined to be approximately 400.1 eV.[21,27] A possible explanation of this new component is instead NH_2 in a different binding configuration compared to A_2. A_1 is not present at the lowest exposures which indicates that it is not related to the most reactive Si(111)7×7 surface sites, or that it relies on already chemisorbed ammonia radicals. The relative intensities at the lowest exposure (0.15 L) reveals an initial inclination for double dissociation of the ammonia molecule, if the assignments above are correct. As the ammonia dose is increased this situation reverses, indicating the presence of more NH_2 than NH on the surface at saturation. This trend was confirmed when a photon excitation energy of 510 eV was used.

Figure 2 shows the normalized integrated N 1s core-level intensity. The most dramatic reduction in intensity takes place between 650 and 750 K, after which the intensity drops to less than half of the initial value. At the same time as the total intensity decreases, intensity is transferred from higher to lower binding energy components [see Fig. 1(b)], i.e., the dissociation progresses. The total loss should correspond to

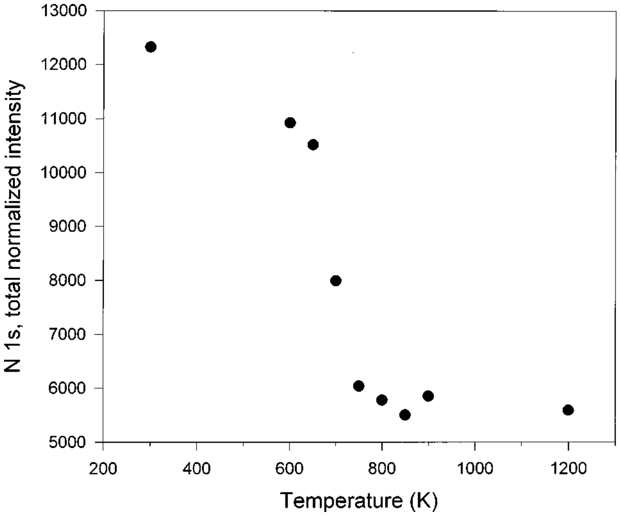

FIG. 2. Integrated and normalized N 1s intensity. With annealing, the intensity of the 5 L exposed surface drops to ~45% of the initial intensity.

diffusion to subsurface positions and/or nitrogen nucleation in some form. Previous desorption studies have not detected nitrogen containing species.[17,26]

Si 2p. Figures 3(a) and 3(b) displays Si 2p core-level spectra at RT and elevated temperatures, respectively. Recent high resolution core-level investigations of Si(111)7×7 (Refs. 7–9) all suggest that the core-level can be divided into one bulk and five or six surface related peaks. To use such a fitting as the starting point for intensity changes and further deconvolution as ammonia dissociates on the surface is extremely difficult and unlikely to give any reliable conclusions. Instead only visually clear changes will be discussed, which means that detailed changes in the main body of the core-level have to be omitted in the discussion. In the clean silicon 7×7 spectrum of Fig. 3(a) the characteristic Si $2p_{3/2}$ restatom contribution on the low binding energy side, denoted S_1, is clearly separable.[7–9] The bulk and other surface related components, including the adatom contribution, overlap in energy, making up the body of the core level.[7–9] When ammonia is adsorbed on the surface the restatom contribution immediately weaken and seems to be completely gone at 0.5 L. On the high binding energy side a new feature D appears already at the lowest coverage. Relying on the concordant fitting procedures for the Si 2p core-level conducted in previous synchrotron PES papers,[7–9] the position of the bulk Si 2p spin-orbit splitted level is located at a binding energy of approximately 99.3 and 99.9 eV for the $2p_{3/2}$ and $2p_{1/2}$ components in our spectra, respectively, with a spin-orbit split of 0.6 eV.[7–9] To separate bulk and surface related components is usually not a problem as the synchrotron provides photons of variable energy, and hence can be operated in a bulk sensitive mode. The $2p_{1/2}$ bulk component is located at 99.9 eV. The $2p_{1/2}$ part of peak D is situated at approximately 101.1 eV, thus shifted ~1.2 eV from the silicon bulk level. Silicon atoms coordinated by four nitrogen atoms have been shown to display a binding energy shift of roughly 2.6 eV to higher energies.[15,18,19,27,32] In an approximative picture where each Si-N bond shifts the binding energy by an equal amount, the D peak would hence correspond to silicon coordinated by two nitrogen and two silicon atoms. An analogous peak from silicon binding to only one nitrogen atom shifted approximately 0.6 eV may exist. It is, however, masked by the body of the core as is silicon binding to one hydrogen atom which should display a similar, although smaller, shift.[33,34]

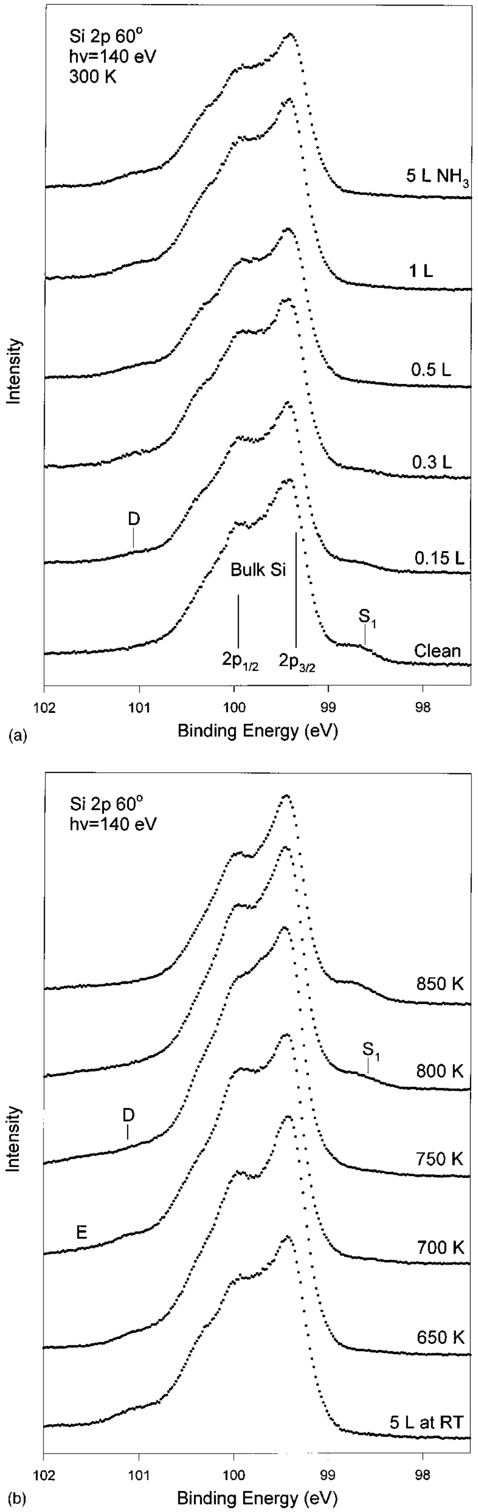

FIG. 3. (a) Silicon 2p core-level spectra of the clean and ammonia reacted surface. The restatom surface state S_1 and the Si^{2+} state D are indicated as well as the position of the bulk 2p components. (b) With annealing intensity is shifted from the Si^{2+} state to higher oxidation states, caption E in the figure. Also, the restatoms recover above 800 K.

In the annealed spectra of Fig. 3(b) the *D* peak, Si^{2+}, gradually decreases in intensity and is very diffuse at 800 K. The restatom contribution, however, is visible only after annealing to 800 K. Thus, the Si^{2+} state appears not to be related to the restatoms. Moreover, starting at 700 K is the appearance of further oxidized silicon states, *E* in Fig. 3(b). Not so much as a clear peak perhaps but certainly as an increase in the background.

VB. Figure 4(a) shows the VB of the clean and RT exposed surface. The clean silicon surface displays the characteristic surface states of the 7×7 surface,[35] where S_1 (0.9 eV) show evidence of the restatom DB's, S_2 (0.3 eV) of adatom DB's and S_3 (1.9 eV), although not clearly resolved in the spectrum, of adatom backbonds. Also indicated in the clean surface spectrum *B* is the silicon bulk transition just below 7 eV.[7,11]

When the clean surface is exposed to ammonia, the well established, both theoretically[36–39] and experimentally,[11,27,41] $3a_1$ and $1e$ molecular orbitals, denoted V_1 and V_2, respectively, develop. The $3a_1$ orbital being composed mainly of nitrogen lone pair electrons and the $1e$ orbital of N-H bonding electrons. The fact that the binding energies of V_1 and V_2 are as low as 4.9 and 10.6 eV, respectively, indicates that they originate from dissociated ammonia species, in a more planar configuration (V_1 close to N $p\pi$) compared with the NH_3 molecule. At the same time the Si-H monohydride bonding feature V_3 is manifested, as intensity start to fill the trench at 5.4 eV.[11,40] Furthermore, there is an apparent shift of the bulk state *B* towards higher binding energy. This is in fact the result of a new peak V_4 at 7.4 eV and associated with N $2p$ and Si $3p$ states.[37–41] The restatom surface state S_1 gradually disappears, to be completely gone at an exposure of 1 L. The adatom related states S_2 and S_3 certainly weaken, but at least the adatom DB's S_2 persists for all exposures. The adatoms are surprisingly thus only partially reacted in the adsorption process, whereas the restatoms all seem to be tied up by ammonia derived species. The higher reactivity of restatoms compared to adatoms seen in STM measurements by Wolkow and Avouris[14,16] is thus confirmed.

When annealed, hydrogen start to desorb from the surface at 650–700 K.[26] This is monitored in Fig. 4(b) by the drop in intensity of the N-H peak V_2 which is not observable above 750 K, and the combined intensity drop/binding energy shift of V_1. The shift towards lower binding energy indicates a higher degree of dissociation, i.e., more nitridelike coordination of the nitrogen atoms. The Si-H feature V_3, however, seems intact at 750 K and weakens at higher temperatures, indicating that hydrogen bonded to nitrogen atoms at the surface desorbs at lower temperatures compared to hydrogen bonded to silicon. The V_4 peak weakens above 700 K in favor of the bulk related peak at slightly lower binding energy. The surface states of the clean 7×7 surface have recovered markedly at 800 K, S_1 and S_3.

The fact that the VB shows the characteristics of silicon nitride V_1, V_2, and V_4 for such low coverages and without annealing, when compared to studies on silicon nitride[41] might seem surprising. But keeping in mind that density of states (DOS) is determined mainly by the short range order, i.e., bond angles, bond distances and coordination number, indicates that the silicon and nitrogen atoms approximates

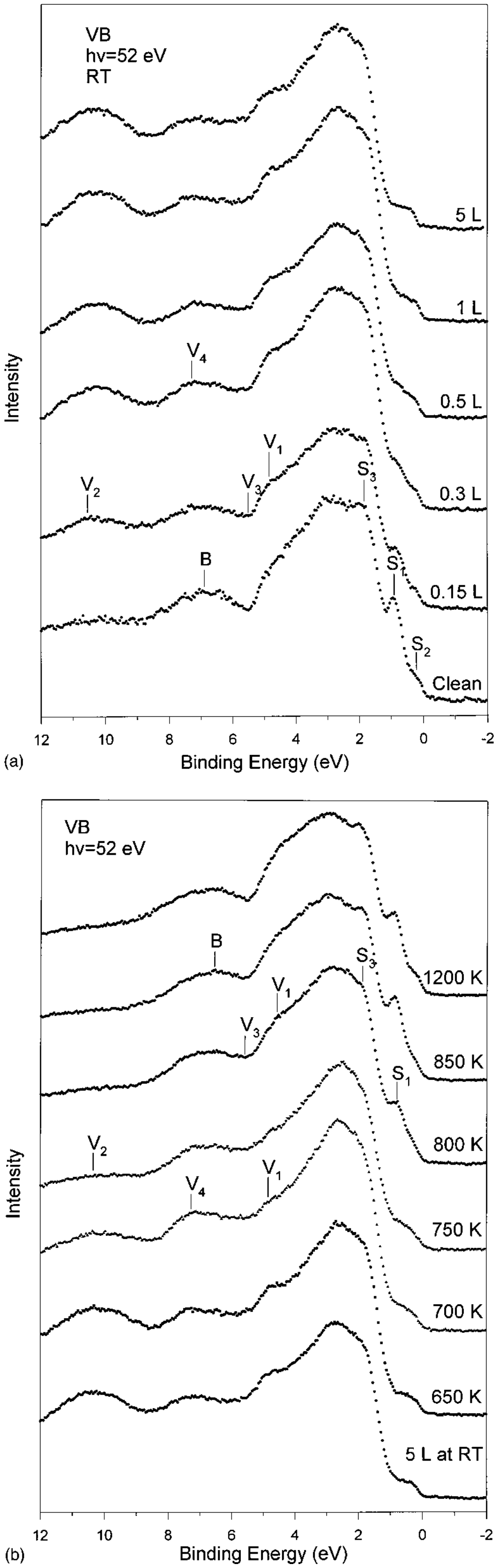

FIG. 4. (a) Valence-band spectra from the clean and reacted surface. Three surface states of the clean 7×7 surface are indicated; S_1 (restatoms), S_2 (adatoms), and S_3 (adatom backbonds), as well as the bulk transition *B* at ~7 eV. The dissociative ammonia chemisorption process induces four new states $V_1 - V_4$ which are identified as nitrogen lone pair, N-H, Si-H, and N $2p$-Si $3p$, respectively. (b) After annealing the surface gradually recovers to be dominated by clean 7×7 surface features.

the bonds in stoichiometric Si_3N_4, i.e., silicon in an almost tetrahedral configuration and nitrogen close to a planar surrounding.

SUMMARY AND CONCLUSIONS

The N 1s core-level shows that the RT dissociative adsorption of ammonia on the Si(111)7×7 surface produces both NH and NH_2 species. The Si 2p spectra also indicates the formation of Si^{2+} states already at the lowest ammonia exposures, which means that Si-Si bonds are indeed broken. The Si-Si bond most likely to be broken is the adatom backbond, which is the surface bond deviating most form the ideal tetrahedral bonding configuration, and thus associated with a great deal of strain as reported previously.[6,42] This mechanism has previously been proposed by Chen, Colaianni, and Yates, Jr.[26,43] after HREELS experiments as the host for NH radicals since two Si DB's are too far apart to be bridged by one NH specie. As for the hydrogen atoms, the annealed VB spectra shows that the recovery of the restatoms coincide with the disappearance of the Si-H bond at 800 K, at which N-H bond features at the surface is already missing in the spectrum. A legitimate picture is thus adatoms with one backbond substituted by a NH radical and its partially filled DB saturated by a NH_2 radical. Moreover, it suggests that H preferentially binds to restatom DB's. This does not necessarily mean that these are the only binding configurations on the surface, but the above described scenario appears to clearly dominate. Although a few earlier important papers[21,26,43] with reports of NH present on the surface have shown gaps in the simple RT dissociation model, the investigation presented in this paper suggests a completely different picture of the dissociation process and its mechanisms. Contrary to most of the previously published studies on this reaction system we can not only say that NH radicals are present, they are also the most abundant ammonia radical in the earlier stage of the adsorption process. This fact must be viewed in a picture where the maximum total energy gained by the system is considered. But, the traditional main driving force, saturation of surface DB's, is a too simple picture to account for the observed surface reactions.

The nature of the new third nitrogen RT core-level component A_1 remains an open question. As mentioned in the discussion part, we do not associate it with physisorbed ammonia since the binding energy is to low, nor do we belief it to be an artifact of the fitting procedure. Asymmetric broadening of the other components can probably not be ruled out in this case with the surface being metallic; however, the component behaves as a true component. The A_1 peak may correspond to NH_2 bonded to adatoms that have not substituted one backbond with a NH radical. We know from STM studies[14,16] that the center and corner adatoms in the 7×7 reconstruction not are electronically equivalent, with a subsequent contrast in reactivity (center adatoms are approximately 4 times more reactive than corner adatoms). Another possibility is thus that the small A_1 component corresponds to NH_2 bonded to the less reactive corner adatom. In fact, a combination of the discussed explanations above could be the case, i.e., NH_2 situated at corner/center adatoms with intact/reacted backbonds.

The VB spectra suggests that the surface adatom DB's are not all reacted in the RT adsorption process. Although it is possible that a new surface state is induced at the same energy by the adsorbates, STM studies[14,16] also indicates that the surface adatoms are only partially reacted in the adsorption process ($\sim50\%$). This seems a rather surprising result since the surface intuitively would cap all DB's with NH_2 or H, especially as there should be more than enough of available hydrogen atoms. Desorption studies show no evidence of H_2 leaving the surface below 650 K.[17,26] However, previous saturation studies indicates that the surface is basically saturated at 1 L,[23] which is also supported by the N 1s spectra in this work [Fig. 1(a)]. The complexity of this reaction system seems further accentuated.

After annealing to 600 K, the dissociation process continues with the appearance of atomic nitrogen at 700 K. At 850 K the nitrogen core-level consists of only atomic nitrogen, and the VB is dominated by the clean 7×7 surface features. The fact that the total nitrogen signal drops to approximately 45% of the initial value indicates that the nitrogen atoms congregates and/or are located below the surface reconstruction as nitrogen species have not been detected in desorption experiments.[17,26]

The 1200 K N 1s core-level reveals a shift of intensity back to higher binding energy as the temperature is high enough for nitrogen and silicon atoms to start to form true silicon nitride complexes, with its characteristic rings of eight or twelve atoms.[3,44] This may explain the presence of peaks $A'5$ and $A'6$, with $A'4$ corresponding to isolated nitrogen atoms, i.e., equal to A_4.

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[1] For a recent review on CVD growth of silicon nitride see, e.g., F. H. P. M. Habraken and A. E. T. Kuiper, Mater. Sci. Eng. R. Rep. **12**, 123 (1994).

[2] *Silicon Nitride and Silicon Dioxide Thin Insulating Films*, edited by V. J. Kapoor and K. T. Hankins (Electrochemical Society, Pennington, NJ, 1987), Vol. 87-10.

[3] A. V. Belyj *et al.*, *Silicon Nitride in Electronics* (Elsevier, Amsterdam, 1988).

[4] K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, J. Vac. Sci. Technol. A **3**, 1502 (1985).

[5] J. E. Northrup, Phys. Rev. Lett. **57**, 154 (1986).

[6] I. Stich, M. C. Payne, R. D. King-Smith, J-S. Lin, and L. J. Clarke, Phys. Rev. Lett. **68**, 1351 (1992).

[7] G. Le Lay, M. Göthelid, T. M. Grehk, M. Björkqvist, U. O.

Karlsson, and V. Yu. Aristov, Phys. Rev. B **50**, 14 277 (1994).

[8] C. J. Karlsson, E. Landemark, Y.-C. Chao, and R. I. G. Uhrberg, Phys. Rev. B **50**, 5767 (1994).

[9] J. J. Paggel, W. Theis, K. Horn, Ch Jung, C. Hellwig, and H. Petersen, Phys. Rev. B **50**, 18 686 (1994).

[10] J. A. Carlisle, M. T. Sieger, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **71**, 2955 (1993).

[11] L. Kubler, E. K. Hlil, D. Bolmont, and G. Gewinner, Surf. Sci. **183**, 503 (1987).

[12] L. Kubler, E. K. Hlil, D. Bolmont, and J. C. Peruchetti, Thin Solid Films **149**, 385 (1987).

[13] F. Bozso and Ph. Avouris, Phys. Rev. B **38**, 3937 (1988).

[14] R. Wolkow and Ph. Avouris, Phys. Rev. Lett. **60**, 1049 (1988).

[15] L. Kubler, J. L. Bischoff, and D. Bolmont, Phys. Rev. B **38**, 13 113 (1988).

[16] Ph. Avouris and R. Wolkow, Phys. Rev. B **39**, 5091 (1989).

[17] B. G. Koehler, P. A. Coon, and S. M. George, J. Vac. Sci. Technol. B **7**, 1303 (1989).

[18] J. L. Bischoff, L. Kubler, and D. Bolmont, Surf. Sci. **209**, 115 (1989).

[19] J. L. Bischoff, F. Lutz, L. Kubler, and D. Bolmont, Thin Solid Films **187**, 101 (1990).

[20] P. Gupta, A. C. Dillon, P. A. Coon, and S. M. Geroge, Chem. Phys. Lett. **176**, 128 (1991).

[21] J. L. Bischoff, F. Lutz, D. Bolmont, and L. Kubler, Surf. Sci. **251/252**, 170 (1991).

[22] A. C. Dillon, P. Gupta, M. B. Robinson, A. S. Bracker, and S. M. George, J. Vac. Sci. Technol. A **9**, 2222 (1991).

[23] S. M. Cherif, J.-P. Lacharme, and C. A. Sébenne, Surf. Sci. **243**, 113 (1991).

[24] J. L. Bischoff, F. Lutz, D. Bolmont, and L. Kubler, Surf. Sci. Lett. **248**, L240 (1991).

[25] S. M. Chérif, J.-P. Lacharme, and C. A. Sébenne, Appl. Surf. Sci. **56-58**, 777 (1992).

[26] M. L. Colaianni, P. J. Chen, and J. T. Yates, Jr., J. Chem. Phys. **96**, 7826 (1992).

[27] G. Dufour, F. Rochet, H. Roulet, and F. Sirotti, Surf. Sci. **304**, 33 (1994).

[28] J. N. Andersen, O. Björneholm, A. Sandell, R. Nyholm, J. Forsell, L. Thånell, A. Nilsson, and N. Mårtensson, Syncrotron Radiat. Res. **4**, 15 (1991).

[29] A. Ishizaka and Y. Shiraki, J. Electrochem. Soc. **133**, 666 (1986).

[30] P. H. Mahowald, D. J. Friedman, G. P. Carey, K. A. Bartness, and J. J. Yeh, J. Vac. Sci. Technol. A **5**, 2982 (1987).

[31] G. Lucovsky, Solid State Commun. **29**, 571 (1979).

[32] D. H. Baek, H. Kang, and J. W. Chung, Phys. Rev. B **49**, 2651 (1994).

[33] K. Hricovini *et al.*, Phys. Rev. Lett. **70**, 1992 (1993).

[34] C. J. Karlsson, F. Owman, E. Landemark, Y.-C. Chao, P. Mårtensson, and R. I. G. Uhrberg, Phys. Rev. Lett. **72**, 4145 (1994).

[35] R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, P. E. S. Persson, and S. A. Flodström, Phys. Rev. B **31**, 3805 (1985).

[36] R. S. Mulliken, J. Am. Chem. Soc. **77**, 887 (1954).

[37] S. Y. Ren and W. Y. Ching, Phys. Rev. B **23**, 5454 (1981).

[38] J. Robertson, Philos. Mag. B **44**, 215 (1981).

[39] J. Robertson, Philos. Mag. B **63**, 47 (1991).

[40] R.-H. Zhou, P.-L. Cao, and S.-B. Fu, Surf. Sci. **249**, 129 (1991).

[41] R. Kärcher, L. Ley, and R. L. Johnson, Phys. Rev. B **30**, 1896 (1984).

[42] J. J. Boland, Surf. Sci. **244**, 1 (1991).

[43] P. J. Chen, M. L. Colaianni, and J. T. Yates, Jr., Surf. Sci. Lett. **274**, L605 (1992).

[44] S. Hampshire, H. K. Park, D. P. Thompson, and K. H. Jack, Nature (London) **274**, 880 (1978).