PHYSICAL REVIEW B VOLUME 38, NUMBER 6 15 AUGUST 1988-II

Photoemission studies of the reactions of ammonia and N atoms with Si(100)-(2×1) and Si(111)-(7×7) surfaces

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(Received 15 January 1988)

We present results of detailed x-ray photoemission and ultraviolet photoemission spectroscopic studies of the reactions of silicon with ammonia and atomic nitrogen. We show that both Si(100)-(2×1) and Si(111)-(7×7) surfaces are very reactive towards ammonia, which adsorbs dissociatively even at 100 K. The extent of dissociation and the dissociation products are different on the two surfaces. On Si(100) the ammonia dissociates to NH while on Si(111) it dissociates to NH_2. On the Si(100) surface the NH species has a lower thermal stability, starting to dissociate at around 500 K. The NH_2 species on Si(111) is stable up to ∼700 K. We explain the above general features in terms of the dangling-bond structure of Si(100)-(2×1) and Si(111)-(7×7) surfaces.

I. INTRODUCTION

The interaction of ammonia with silicon surfaces at high temperatures (1200–1500 K) has been extensively studied in the past, mainly due to the interest in silicon nitride film growth by thermal nitridation.[1] Recently, there has been an increased interest in similar studies at lower temperatures (100–700 K), for the purpose of understanding the silicon-ammonia interaction at an atomic level, and to understand and relate the reactivity of silicon to its surface electronic structure.[2–6] A further motivation for detailed study is the need emerging in the microelectronics technology for nonthermal ways of thin film growth and processing.[7]

This new interest has already been reflected in a number of recent attempts to form silicon nitride at low temperatures by electron-beam-induced,[2,8–10] synchrotron-radiation-induced,[11] and excimer-laser-enhanced[12] nitridation. A fundamental question involves the role of surface electronic structure and reconstruction in the extent and nature of the silicon-ammonia reaction. At low temperatures, where the thermal activation of reactions is low, the reactivity of the surface more directly reflects electronic factors. In previous work on the low-temperature reactivity of the Si(100)-(2×1) surface, we stressed the important role of dangling-bond surface states and their ability to dissociate nitric oxide and to break N—H bonds in ammonia even at 90 K.[2,10] In more recent work[4,5] it was confirmed that NH_3 dissociates on both Si(100) and Si(111) surfaces at room temperature. However, the same authors were unable to observe dissociative adsorption at 100 K. In yet another work[6] it was concluded that on the Si(111)-(2×1) surface ammonia adsorbs for the most part nondissociatively.

In this paper we present the results of detailed x-ray photoemission (XPS) and ultraviolet photoemission (UPS) spectroscopic studies of the reaction of silicon with ammonia and atomic nitrogen. These studies resolve the existing ambiguities and provide new insight into the electronic factors that control low-temperature reactivity. They show that both Si(100)-(2×1) and Si(111)-(7×7) surfaces are very reactive towards ammonia, which adsorbs dissociatively even at 100 K. However, both the extent of the dissociation and the nature of the dissociation products are different at the two surfaces. On the Si(100) surface, NH_3 dissociates to $NH + 2H$ with both products bonded to Si atoms, while on Si(111) it dissociates to $NH_2 + H$. The NH species has a low thermal stability, starting to dissociate at around 500 K. The NH_2 species on Si(111) is, however, stable up to ∼700 K. We show that the above general features can be accounted for in terms of the different dangling-bond structure of the Si(100)-(2×1) and Si(111)-(7×7) surfaces.

II. EXPERIMENT

The experiments were performed in an ultrahigh-vacuum (UHV) system with a base pressure of 7×10^{-11} torr. This system was equipped for XPS, UPS, Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), ion-scattering spectroscopy (ISS), thermal-desorption spectroscopy (TDS), and electron-stimulated desorption (ESD). The samples were mounted on a liquid-nitrogen-cooled sample holder, which, combined with resistive sample heating, ensured very clean operating conditions. The pressure in the system did not exceed 5×10^{-10} torr at sample temperatures as high as 1100 K. The Si(100) was *n*-type, phosphorous doped 10 Ω cm and the Si(111) was *p*-type boron doped 10 Ω cm material. The binding energies in the XPS and UPS are referred to the valence-band maximum of the clean samples. The UPS spectra were taken using He II (40.8 eV) radiation. Sample cleaning and high-quality Si(100)-2×1 and Si(111)-7×7 surfaces were achieved by 2 keV Ar^+ bombardment followed by short (60 sec) annealing to 1100 K and rapid cooling (∼150 sec) to 100 K. The cleanliness of the samples was monitored by UPS with a sensitivity far exceeding that of XPS or AES. The experiments were performed by exposing the samples to ammonia at 100 K, followed by stepwise annealing to ∼300, ∼700, and ∼950 K. UPS and XPS spectra were taken at 100 K after each step.

In the XPS study of ammonia adsorption on a defect-rich Si(100) surface, the sample was not annealed after the usual cleaning procedure with 2-keV argon ions. For a UPS study of an atomic-nitrogen-exposed surface, the sample was exposed to a beam of nitrogen from the ion gun operated with the beam voltage turned off.

We note that although we used ND_3 in our experiments, in the discussion we use NH_2 and NH instead of ND_2 and ND in order to conform with the assignments used in the literature for relevant species of the Si-NH_3 interaction.

III. RESULTS AND DISCUSSION

A. The reactions of ammonia with Si(100) and Si(111)

1. *Core-photoemission results*

In Figs. 1(a) and 1(b) N (1*s*) XPS spectra of perfect and ion-bombardment Si(100) surfaces are shown after ammonia adsorption at 100 K and after subsequent annealing steps. The samples were exposed to 5 langmuirs (L) of ammonia (5 L$=5\times10^{-8}$ torr for 100 sec); thereafter the ammonia was evacuated. A spectrum of the perfect Si(100) was also taken in 5×10^{-9} torr ammonia after the 5 L exposure, which sustained a higher ammonia adsorption equilibrium (curve *A*′). On both perfect and sputtered surfaces at 100 K the spectrum is composed of two peaks, indicating the presence of different NH_x species. The peak with a binding energy (BE) of 400.1 eV is related to physisorbed molecular ammonia. This peak disappears and reappears upon increasing the temperature to only 200 K or reexposing the sample to ammonia at 100 K. The other peak is more apparent after annealing to 300 K (curve *B*), i.e., after desorption of the molecular ammonia, as observed by TDS in addition to XPS. On the Si(100) surface this peak is at 398.5 eV. A N (1*s*) XPS peak of the same position and intensity resulted after 5-L ammonia exposure at 300 K [Fig. 1(a), curve *B*′]. Further annealing to a higher temperature resulted in broadening of the 398.5-eV peak toward lower BE (not shown in Fig. 1), indicating some conversion of this species. Upon annealing to 950 K the formation of a new species was evident by a distinct new peak at 397.7 eV. The binding energy of this peak is the same as the one in a thin silicon nitride film prepared by thermal nitridation of Si(100) in reaction with 4 L ammonia at 975 K. The formation of silicon nitride under such conditions is evidenced by its UPS spectrum [shown in Fig. 6(b)]. Therefore the 397.7-eV peak is due to atomic nitrogen reacted with silicon which results from the complete dissociation of the NH_x intermediate at 398.5 eV BE. The 398.5-eV peak could consequently be due to either NH_2 or NH.

XPS spectra of the ammonia-exposed Si(111) surface, shown in Fig. 2, can help determine the exact nature of the NH_x species. At 100 K, the spectrum of the

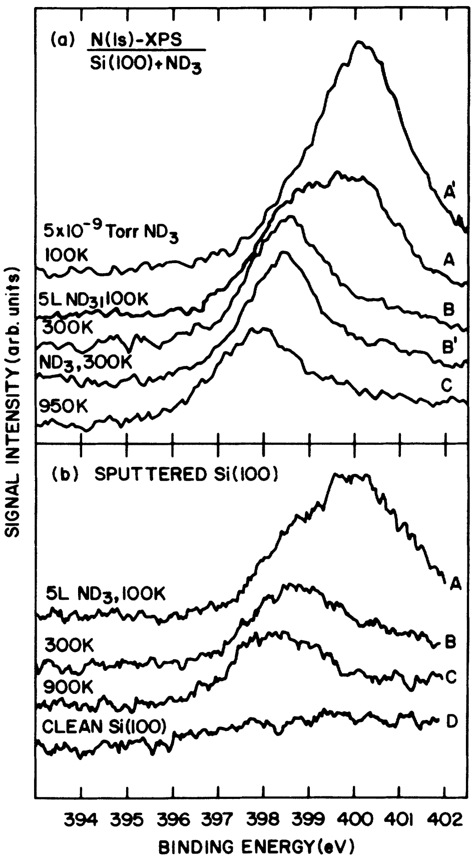

FIG. 1. N (1*s*) XPS spectra of a Si(100)-(2×1) surface exposed to 5 L ammonia at 100 K (curve *A*), after annealing to 300 K (curve *B*) and after annealing to 950 K (curve *C*). Curve *A*′: In 10^{-9} torr ammonia following 5-L exposure at 100 K. Curve *B*′: After 5 L exposure at 300 K. (b) N (1*s*) XPS spectra of a sputtered Si(100) surface exposed to 5 L ammonia at 100 K (curve *A*), after annealing to 300 K (curve *B*) and after annealing to 950 K (curve *C*). Curve *D*: Clean sputtered Si(100).

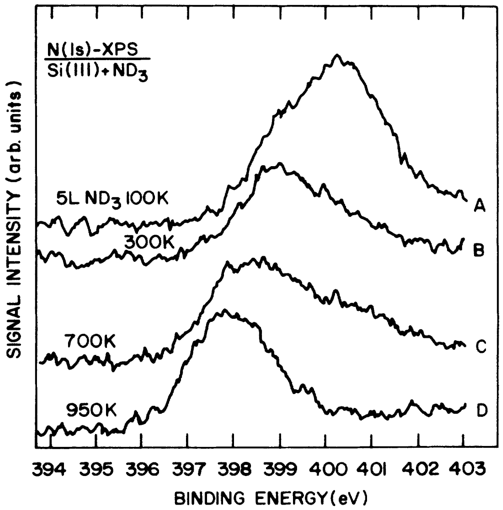

FIG. 2. N (1*s*) XPS spectra of a Si(111)-(7×7) surface exposed to 5 L ammonia at 100 K (curve *A*), after annealing to 300 K (curve *B*), after annealing to 700 K (curve *C*) and after annealing to 950 K (curve *D*).

ammonia-exposed Si(111) (curve *A*) again reflects the existence of two different species, of which the one at 400.1 eV can be identified as physisorbed molecular ammonia, as on the Si(100) surface. The second peak at 398.8 eV emerged after annealing to 300 K (curve *B*). This BE is 0.3 eV higher than on the Si(100) surface. The annealing to 700 K resulted in only a small shift to lower BE (curve *C*). The leading edge and the shape of the spectrum suggest that the species responsible for the 398.8-eV peak is converted to a small extent into the species giving the 398.5-eV peak. This species, on the other hand, was present on the Si(100) surface at a much lower temperature (300 K). Upon annealing to 950 K this peak shifted to 397.6 eV [as in the case of the Si(100) surface] but still retained some contribution from the higher BE band (curve *D*). At this point it can be concluded that there are two identical species on both surfaces, i.e., molecular ammonia with 400.1 eV and N bonded to silicon with 397.7 eV N (1*s*) BE. Furthermore, there is a species with a BE of 398.5 eV on Si(100) and 398.8 eV on Si(111), which may tentatively be assigned as NH and NH_2 surface species produced by the dissociation of ammonia. The XPS spectra of the ammonia-exposed Si surfaces reflect a behavior resembling that of similarly treated transition-metal surfaces. Photoemission studies have shown that on one group of transition-metal surfaces, which includes Ni(100),[13] Ni(111),[14] Fe(100), and Fe(111),[15] molecular ammonia coexists with mainly NH_2 up to ~300 K, while on Ni(110),[16] Fe(100),[17] and W(110) (Refs. 18 and 19) the NH dissociation product is predominant. On silicon surfaces Kubler *et al.*[4,5] reported the dissociative adsorption of ammonia and the formation of unidentified NH_x species at 300 K. The NH_x species were characterized by a 398.5 eV BE on Si(100)[3] and 398.4–398.6 eV on Si(111).[4,5] At higher temperatures the formation of an atomic nitrogen species with 397.4 eV BE was evident. On the one hand, these findings are in agreement with our results, on the other hand, however, these authors could see only molecularly adsorbed ammonia at 100 K characterized by 400 eV N (1*s*) BE. This observation was made, however, with a silicon sample that could not be annealed but only ion etched at room temperature and cooled to 100 K for the experiments. In the absence of any other contamination, the sample prepared in this way may have been hydrogen passivated. We could observe a high amount of hydrogen in the surface layer of some freshly ion-bombarded silicon by ESD and TDS. Our XPS spectra show that not only on perfect Si(100)-(2×1) or Si(111)-(7×7) but also on ion-bombardment Si(100) [Fig. 1(b)] ammonia is partially dissociated at 100 K. Further evidence supporting this will be presented during the discussion of UPS spectra. Moreover, we observe that between the 400.1-eV BE peak due to molecular ammonia and the 397.7-eV BE peak due to nitrogen in silicon nitride, two different NH_x species exist with 398.5 eV on Si(100) and 388.8 eV N (1*s*) BE on Si(111), respectively. Since on Si(111) we saw some conversion of the 398.8-eV species into the 398.5-eV species upon heating, we tentatively assign the former to NH_2 and the latter to NH. These conclusions receive further support from valence photoemission studies.

2. *Valence-photoemission results*

In Fig. 3 curve *A* shows the UPS spectrum of the Si(100) surface exposed to 5 L ammonia at 100 K. The spectrum has two peaks at 5.7 and 11 eV, thus giving a peak separation of 5.3 eV. The UPS spectrum of gas-phase (or condensed) ammonia has two electronic levels in the same energy range, the $3a_1$ nitrogen lone-pair orbital at 11.1 eV and the 1*e* N—H bonding orbital at 16.4 eV below the vacuum level.[20] Kubler and co-workers[3] found binding energies of 5.85 and 11.1 eV for the same orbitals in physisorbed ammonia on silicon at 100 K, with reference to the Fermi level. In Fig. 3 the peaks at 5.7 and 11 eV below the valence-band maximum have practically the same $3a_1$ and 1*e* BE values as in gas or physisorbed phases, therefore they indicate molecular ammonia at 100 K. Under similar conditions, however, XPS showed the presence of NH_x fragments and approximately one monolayer of physisorbed ammonia. The presence of NH_x fragments is more apparent in UPS after annealing to 300 K (curve *B*). Spectrum *B* shows a new peak at 7.2 eV, while the other two peaks shifted to lower BE at 4.4 and 10.4 eV, giving a peak separation of 6 eV compared to 5.3 eV in physisorbed ammonia. Upon further annealing to 700 K, spectrum *C* evolved which resembles silicon nitride, as we later show. On transition-metal surfaces it is well known that upon molecule chemisorption the $3a_1$-1*e* separation is reduced by over 1 eV due to the preferential bonding shift of the $3a_1$ lone-pair level to higher BE.[14,16] Since the chemisorption bond is formed by participation of the lone-pair orbital of the ammonia without significant involvement of the 1*e* orbitals, the result of molecular chemisorption on silicon as well should be the shift of the $3a_1$ level to higher BE, thereby decreasing the $3a_1$-1*e* separation. Contrary to

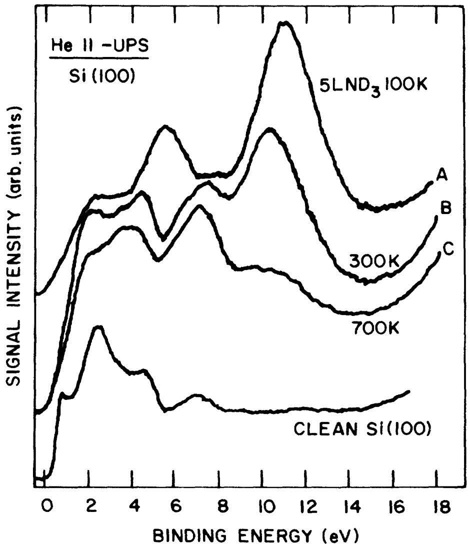

FIG. 3. He II UPS spectra of a Si(100)-(2×1) after 5 L ammonia exposure at 100 K (curve *A*), after annealing to 300 K (curve *B*), after annealing to 950 K (curve *C*).

this, our observation of increased separation of these levels on Si together with the appearance of a new emission band at 7.2 eV implies the presence of surface species other than molecular ammonia. The question is then, whether these features indicating the dissociation of ammonia are the result of annealing to 300 K, or were they present at 100 K but suppressed by a much higher emission intensity from coadsorbed molecular ammonia. Photoemission spectra of the Si(100) surface exposed to submonolayer amounts of ammonia clearly indicate partial dissociation at 100 K. In Fig. 4 we show UPS spectra of the clean Si(100) (curve *A*), after 5, 0.1, and 0.4 L ammonia adsorption at 100 K (curves *B*, *C*, and *E*), after atomic hydrogen adsorption (curve *D*) and after annealing to 300 K following the 5 L ammonia adsorption at 100 K (curve *F*). The spectrum after 0.1 L ammonia adsorption shows two bands at 10.4 and 12.4 eV, i.e., on both sides of the molecular ammonia 1*e* band at 11 eV. The 10.4 eV band coincides with the pronounced peak after the 300 K annealing, the 12.4 eV band coincides with a hydrogen-induced band (curve *D*) on a surface exposed to atomic hydrogen. An emission band coinciding with the 7.2 eV peak of the annealed sample is discernible on both the 0.1 and 0.4 L ammonia-exposed surfaces. The UPS results therefore support the presence of NH_x species, i.e., the breaking of ammonia N—H bonds not only after annealing but at 100 K as well.

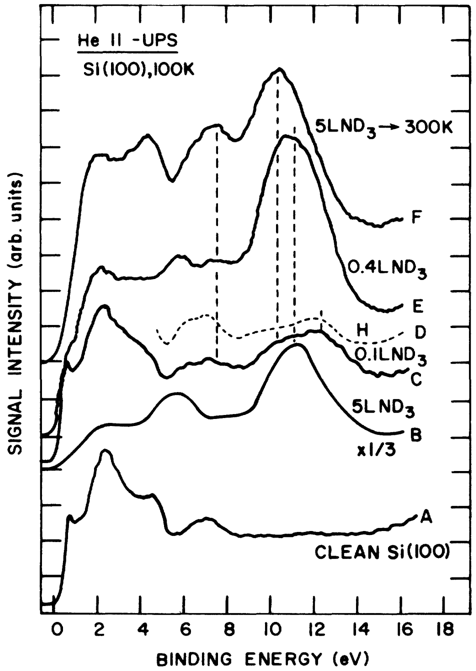

FIG. 4. He II UPS spectra of ammonia- and atomic-hydrogen-exposed Si(100). Curve *A*: Clean Si(100). Curve *B*: After 5 L ammonia exposure at 100 K. Curve *C*: After 0.1 L ammonia exposure at 100 K. Curve *D*: After exposure to atomic hydrogen at 100 K. Curve *E*: After exposure to 0.4 L ammonia at 100 K. Curve *F*: Annealed to 300 K after exposure to 5 L ammonia at 100 K.

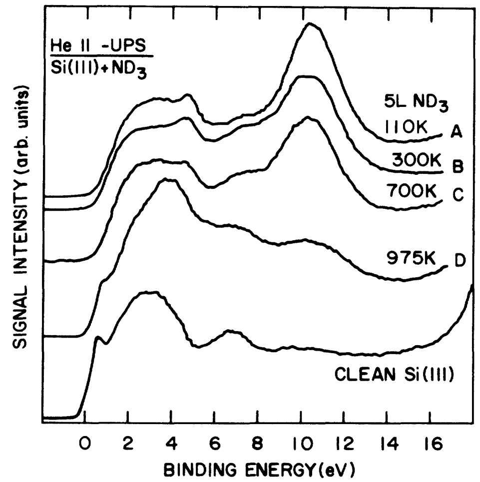

FIG. 5. He II UPS spectra of a Si(111)-(7×7) exposed to ammonia at 110 K (curve *A*), after annealing to 300 K (curve *B*), after annealing to 700 K (curve *C*) and after annealing to 975 K (curve *D*).

UPS spectra of the ammonia-exposed Si(111) surface are shown in Fig. 5. The lowest temperature attained in this experiment was 10 K higher than with Si(100), therefore the physisorbed ammonia coverage is expected to be lower. After 5 L ammonia exposure at 110 K the spectrum of the Si(111) surface showed three peaks at 4.6, 7.2, and 10.4 eV (curve *A*). The UPS spectrum did not change significantly upon annealing to 700 K, except for an apparent increase in the 7.2 eV peak intensity. At 300 K the difference in the spectra on the two surfaces is, that on Si(111) the 4.6 eV peak is at 0.2 eV higher energy and the 7.2 eV peak is less intense than on Si(100). The $3a_1$-$1e$ peak separation is 5.8 eV, thus excluding the assignment of the UPS features to molecular ammonia on Si(111) as well.

Based on the fact that upon annealing to 700 K, the intensity of the 7.2 eV UPS and 398.5 eV XPS peaks on Si(111) increased and both of these peaks were characteristic of NH_x species on the Si(100) surface, further support is given to our conclusion that the dissociation product is NH_2 on the Si(111) and NH on the Si(100) surface. Dissociative chemisorption and the formation of NH_2 species at 300 K on the Si(111)-(7×7) surface is also confirmed by the very recent high-resolution electron-energy loss (EELS) studies of Tanaka *et al.*[21] We note here that based on isotope effect studies performed in the above work,[21] the assignments used to claim a molecular adsorption of NH_3 on Si(111)-(2×1) are in error in the work of Kilday *et al.*[6] Their results can also be interpreted (see assignments in Ref. 21) in terms of dissociative chemisorption and formation of NH_2 species at 300 K.

B. The reaction of N atoms with Si(100)

In order to understand the UPS spectra observed after annealing to higher temperatures, we exposed the Si(100) surface to an atomic nitrogen beam at 90 K. The UPS spectra after N exposure and after annealing to 400 and

1100 K are shown in Fig. 6(a). At 90 and 400 K spectra *A* and *B* showed peaks at 4.3, 7, and 11.2 eV. Upon annealing to 1100 K the known silicon nitride spectrum evolved with characteristic peaks at 4.2, 7.2, and 11.2 eV. The 4.2 eV peak is due to the nonbonding N2p_π level. The peaks at 7.2 and 11.2 eV are due to N(2$p_{x,y}$)—Si(3p) and N(2$p_{x,y}$)—Si(3s) bonding levels, respectively.[23] At 90 and 400 K, which are well below the temperature of silicon nitride formation, the observed spectral features are expected to reflect electronic states related to Si—N bonding levels, nitrogen and silicon dangling bonds, and nitrogen nonbonding orbitals. Robertson has calculated the electronic levels associated with nitrogen and silicon dangling bonds in silicon nitride.[24] According to these calculations, the N dangling bond is a *p* orbital lying in the nonbonding N2p_π valence band of silicon nitride. Indeed, the 4.3 eV peak in spectra *A* and *B* lines up with the N2p_π band in spectrum *C*, supporting a N dangling-bond origin. It is straightforward then to assign the 7.2 and 11.2 eV peaks to N(2p)—Si(3p) and N(2p)—Si(3s) bonding levels. On ammonia-exposed surfaces the 4.4, 7.2, and 10.4 eV UPS peaks are at very similar positions, a fact which suggests electronic levels similar to those of the N-exposed surface. Assuming that NH species are present on the surface of Si-(100) these three photoemission bands may be attributed to N nonbonding and dangling-bond states, Si(3p)—N(2p), Si(3s)—N(2p) bonding states, and N—H and Si—H bonding states, respectively. Earlier we have seen that the N2p_π nonbonding level and the N(2p) dangling-bond state are at nearly the same energy at ~4.3 eV. Kärcher *et al.* observed[23] that the lone-pair BE was unaffected by hydrogen in hydrogenated SiN$_x$. Therefore the 4.4 eV peak can be assigned either to a dangling bond or a nonbonding state of NH bonded to one or two silicon atoms. The 7.2 eV peak of the NH$_3$-exposed Si(100) surface is again at almost the same energy as the Si(3p)—N(2p) bonding level (7 eV) in the UPS spectra of the N-exposed and annealed Si(100) or of Si$_3$N$_4$. The dissociation of ammonia implies, most importantly, the formation of a Si—N bond, i.e., a Si(3p)—N(2p) bonding level. The work of Kärcher *et al.* showed[23] that the Si(3p)—N(2p) bonding level is practically at the same energy in SiN$_x$ and in hydrogenated SiN$_x$-H. Ir spectra of similarly prepared samples show Si-NH groups.[25] This provides further support to the proposal that the Si(3p)—N(2p) bonding level as well is at a similar energy in Si-N and Si-NH. We suggest therefore that the 7.2 eV peak in the UPS spectra is indicative of dissociative adsorption of ammonia and can be associated with the presence of the NH fragment. A Si(3p)—H(1s) bonding state as the origin of the 7.2 eV peak is not likely because such a peak would be centered at ~6 eV, based on our UPS spectra of H and Si$_2$H$_6$-exposed Si(100) and Si(111) surfaces.[26] The 10.4 eV band is most likely a composite of Si(3s)—N(2p), Si(3s)—H(1s), and N—H bonding levels.

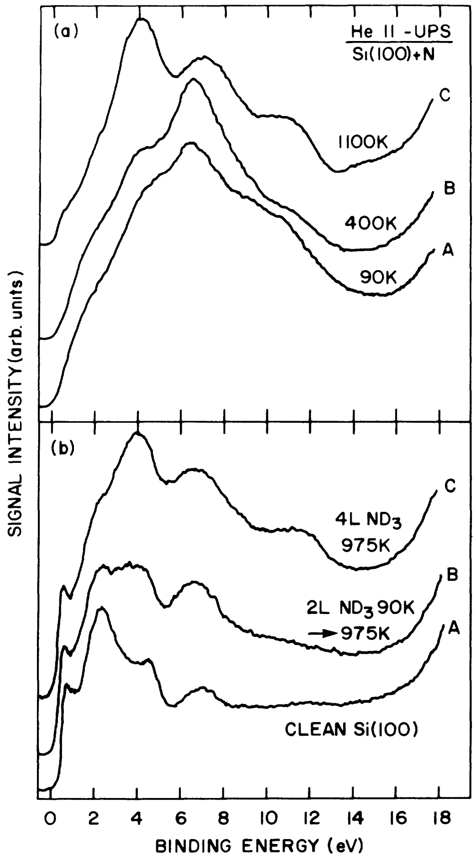

FIG. 6. (a) He II UPS spectra of an atomic-nitrogen-exposed Si(100)-(2×1) surface at 100 K (curve *A*), after annealing to 400 K (curve *B*) and after annealing to 1100 K (curve *C*). (b) He II UPS spectra of clean Si(100)-(2×1) (curve *A*), after exposure to 2 L ammonia at 90 K and annealed to 975 K (curve *B*) and after exposure to 4 L ammonia at 975 K (curve *C*).

In Fig. 6 another interesting feature can be observed. Exposing the Si(100) surface at lower temperatures (100–300 K) to ammonia or atomic nitrogen results in elimination of the dangling-bond surface electronic states. However, after annealing of the atomic-nitrogen-exposed surface to 1100 K, or after reaction with ammonia at 975 K, the presence of dangling-bond states is apparent in spite of clear evidence of silicon nitride formation. The presence of the surface states implies that even under such conditions the surface layer of the sample must be of silicon. This is in agreement with our earlier observation by ISS,[2,10] that the topmost atomic layer of the ammonia-reacted silicon surface is silicon and the nitrogen occupies subsurface sites.

IV. SUMMARY AND CONCLUSIONS

From the experimental results presented above we have seen that the low-temperature reactivity of silicon surfaces towards NH$_3$ is high and that both Si(100)-(2×1) and Si(111)-(7×7) surfaces can dissociate NH$_3$ at temperatures as low as 100 K. There are, however, differences in the reactivity of the two surfaces. The Si(100)-(2×1) surface is more reactive, being able to dissociate NH$_3$ to NH + 2H, while on Si(111)-(7×7) only one N—H bond is broken to give NH$_2$ + H. This difference in reactivity can be understood by reference to the surface electronic structure of Si(100)-(2×1) and Si(111)-(7×7) surfaces. In the dimer model[27] on the 2×1 reconstruction of Si(100), alternate rows of surface silicon atoms move towards each other to form Si-Si dimers. In the dimerized surface there is still one dangling bond per surface Si atom. This high dangling-bond density is responsible for the high reactivity of the Si(100) surface. Moreover, not only the number of dangling bonds but also their spatial distribution is important in the Si-NH_3 reaction. Since each atom in the Si-Si dimer possesses a dangling bond, and the Si—Si bond distance is similar to the H-H distance in NH_3, a concerted hydrogen-abstraction reaction can take place where two H atoms are abstracted from a single NH_3 molecule. Such a process would lead to the production of NH and the saturation of both dangling bonds by hydrogen, in agreement with our findings here. Of course, single H abstraction can also take place. We have recently studied the Si(100) + NH_3 reaction with scanning tunneling microscopy (STM).[28] The STM results clearly show that at 300 K the reaction preserves the Si—Si dimer bond and thus is limited to saturating the existing dangling bonds. The fact that STM line scans indicate that most of the dimers on the NH_3-exposed surface are symmetrically terminated, along with spectroscopic evidence for surface Si—H bonds, supports the picture in which the simultaneous two hydrogen abstraction is the dominant reaction mechanism on the Si(100) surface. Unlike a previous suggestion[3] we observe very few SiH_2 groups with the STM on the reacted surface at 300 K. As we saw above, on the Si(111)-(7×7) surface the main ammonia dissociation product is NH_2. Moreover, this species is stable on the Si(111)-(7×7) surface up to 700 K.

Unlike the Si(100)-(2×1) surface, the dangling-bond density on Si(111)-(7×7) is very low. Of the 49 dangling bonds present on the bulk-terminated Si(111) surface only 19 survive the 7×7 reconstruction. The dangling bonds are more apart on the 7×7 surface so that double H abstraction is not feasible, a fact which explains the predominance of NH_2 fragments and their high thermal stability. In recent STM studies of the Si(111) + NH_3 reaction[29,30] we found that, as in the case of Si(100), the room-temperature reaction preserves the surface reconstruction, a fact which shows that the reaction limits itself to the dangling-bond sites. These STM studies also showed that on the Si(111) surface not all dangling-bond sites are chemically equivalent but subtle electronic effects such as charge transfer between sites can further influence the low temperature reactivity of Si surfaces. The UPS studies of the N-atom-exposed Si surfaces help us assign the electronic levels of the ammonia-exposed surfaces. It is also interesting that the surface dangling-bond bands are present on the N-atom-exposed and annealed silicon surfaces. This observation corroborates our earlier proposal based on ion scattering[2,10] that the nitrogen atoms in thin silicon nitride films occupy mainly subsurface sites.

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