Photoemission study of ammonia dissociation on Si(100) below 700 K

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Ultraviolet and x-ray photoelectron spectroscopies (UPS and XPS) have been used to study the initial NH_3 adsorption stage on the Si(100)-2×1 surface between room temperature (RT) and 700 K. Our results are markedly different from recently reported data, showing complete NH_3 dissociation and surface dangling-bond (DB) saturation with H adatoms even below RT. While UPS features relevant to Si—H bonds (in dihydride at RT and monohydride near 600 K) are actually observed, other coadsorbed species labeled NH_X are clearly identified in our photoemission experiments and contribute to the surface passivation. Thus only partial dissociation of NH_3 occurs on Si(100) at least up to 550 K, and the initial thermal nitridation is not just rate limited by surface DB saturation with H. The present findings allow new insights into the mechanism of electron-beam-assisted nitridation at low temperature.

I. INTRODUCTION

Mainly used in the semiconductor technology for high temperature ($T > 1000$ K) CVD silicon nitride depositions, NH_3 would also possibly be an interesting candidate for thin nitride layer growth by thermal nitridation. In this respect a study of the interaction of NH_3 with low index Si surfaces using surface techniques is of great concern. Clearly, much may be learned from such investigations about the mechanism limiting nitridation at low substrate temperature (T_s). We have employed ultraviolet (UPS) and x-ray (XPS) photoemission spectroscopy to study the chemisorption of NH_3 on Si(100) at low T_s (300 K $< T_s <$ 700 K). To our knowledge no UPS study of this system has been reported. Our investigation complements recent work by Glachant and Saidi,[1] Bozso and Avouris,[2] as well as our own work[3] dealing with chemisorption of NH_3 on Si(111). Both XPS and UPS data provide new insight into the surface dangling-bond (DB) passivation mechanism, markedly different from that proposed in Ref. 2. These authors, on the basis of (i) the XPS observation at 90 K of two distinct N_{1s} peaks [at 399.7-eV binding energy (BE) relevant to molecular adsorption and at 397.7 eV attributed to nitrogen from completely dissociated molecules] and (ii) the presence of chemisorbed hydrogen observed in a rather indirect way by thermal desorption experiments (TDS) and inelastic background variations in ion scattering spectroscopy (ISS), conclude that there is a self-limiting complete dissociation of NH_3 on the surface already at 90 K with a subsequent hydrogen saturation of the surface DB's. This latter DB passivation with hydrogen would inhibit further NH_3 dissociation. Although we did indeed detect hydrogen adsorption below 550 K, we show in this Rapid Communication that DB passivation by Si—H bonds is only partial and that coadsorption of hydronitrided NH_X species also occurs in this T_s range and contributes significantly to the surface passivation.

II. EXPERIMENT

This experiment was performed in an ultrahigh vacuum (UHV) chamber with a 2×10^{-10}-mbar base pressure.

The substrates were nearly intrinsic (p-type 10 Ω cm)c-Si(100) wafers. The temperature T_s was varied by direct Joule heating and measured with a chromel-alumel thermocouple. Clean c-Si(100)-2×1 reconstructed surfaces were generated by repeated cycles of Ar$^+$ sputtering and annealing at 1100 K. No O, N, or C impurities were detectable by XPS. Using another substrate holder, which can be cooled down to 100 K but not heated above room temperature (RT), we also condensed ammonia on a Si surface (amorphized by ion etch cleaning) at $T_s \sim 100$ K. More experimental details are given in previous publications.[3,4]

III. RESULTS

1. XPS

In Fig. 1 we compare the N_{1s} core line evolution with T_s for Si(100) exposed to 10 L (1 L $= 10^{-6}$ Torr sec) of NH_3. The BE behavior is roughly similar to that reported for other surfaces such as c-Si(111)-(7×7)[3] and for amorphous deposited films.[4] Three essential features can be observed, reflecting three different local chemical environments.

At very low T_s (100 K) the line a at 400.0-eV BE is attributed to molecular condensation on the amorphized substrate. It grows very rapidly with exposure, denoting a very high sticking coefficient, and shifts for higher coverages to higher BE's, because of increasing sample charging.

At high T_s ($T_s > 550$ K) a component β at low BE (397.4 eV) becomes apparent. According to previous investigations[3,4] this form of nitrogen is attributed to chemisorbed atomic species coming from completely dissociated NH_3. These adatoms are expected to be more strongly bound to the substrate than any other partial dissociation product NH_X ($X = 1,2,3$). This might explain why atomic nitrogen is associated with the lowest BE since the relevant extra-atomic relaxation energy should be the highest among all NH_X species ($X = 0,1,2,3$) chemisorbed on Si(100). The rapid increase of the β line by raising the temperature above 700 K at constant exposures (spectra e–g in Fig. 1) proves the connection between line

β and the formation of nitride environments $(Si)_3 \equiv N$ during the thermal nitridation. But as the nitride layer becomes thicker (spectrum g, Fig. 1), the line β shifts somewhat to higher BE's probably because of differences in relaxation energies when the matrix surrounding the local nitride environment changes from a semiconducting to an insulating one. This fact may explain some discrepancies in the reported BE values for N_{1s} in this configuration and possible neglect of or confusion with the intermediate γ line.

In contrast to the two previous lines, a rapid saturation coverage can be achieved for the 398.5-eV line, labeled γ, with a few L (~ 10 L) in agreement with the UPS data. The saturation coverage reaches ~ 0.25 ML if we assume a density of 6.8×10^{14} atom cm^{-2} at monolayer completion (the 100 plane density). Moreover, the adsorbed amount in this intermediate form γ decreases between RT and 600 K. In their letter Bozso et al.[2] did not give XPS spectra in the RT range. Peaking 2 eV below the molecular BE contribution, their second line, observed at 90 K, can hardly account for the nitride environment observed in our work
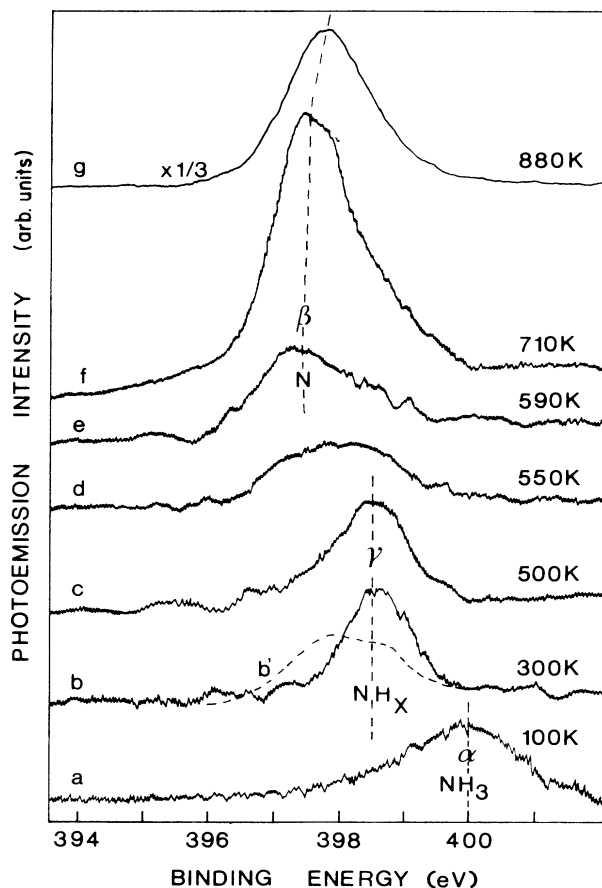
above 550 K only and showing a BE difference of 2.6 eV with the molecular contribution $(\beta\text{-}\alpha)$.

2. UPS

Figure 2 summarizes the UPS data for NH_3 adsorbed on Si(100) as a function of T_s. Trace b corresponds to low T_s (~ 100 K) NH_3 condensation. The two NH_3 induced features at ~ 5.85 and ~ 11.1 eV are usually assigned to the $3a_1$ and $1e$ molecular orbitals composed of the nitrogen lone pair and the N—H bonding states, respectively.[5,6] It can be seen in spectra c and d in Fig. 2 that the UPS spectrum for T_s between RT and 500 K closely resembles the low T_s spectrum. Two sharp features centered now at 4.8 and 10.4 eV can be attributed to chemisorbed species. These peaks saturate at 10-L exposure
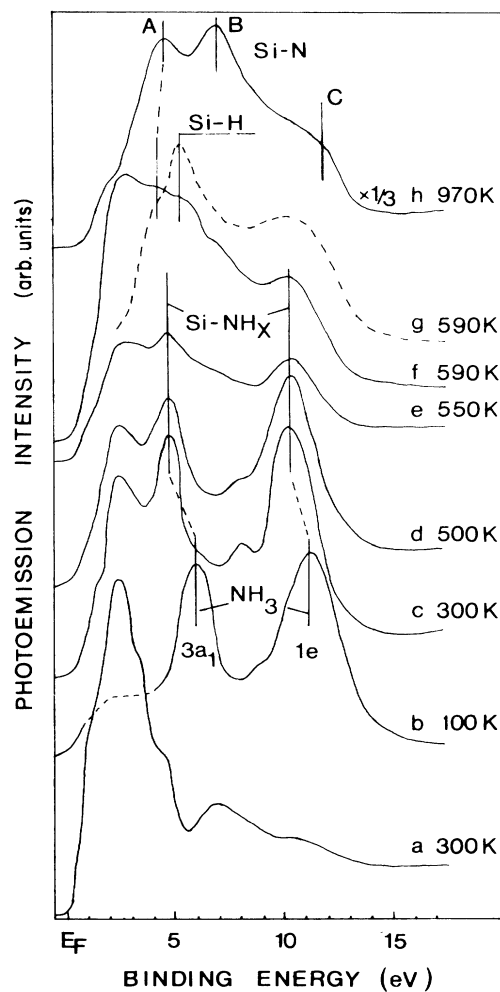

FIG. 1. XPS $N(1s)$ core-level spectra as a function of T_s at constant NH_3 exposures (10 L) except for spectrum a which corresponds to NH_3 condensation at 100 K described in spectrum b in Fig. 2. The dashed line (b') accounts for the RT exposure (b) but bombarded by an Ar$^+$ ion pulse (15") ($\sim 5 \times 10^{14}$ ions/cm^2) ($E = 2$ keV).

FIG. 2. He II (40.8-eV) photoelectron spectra at emission angle $\theta = 60°$. a: Clean c-Si(100-(2×1)) substrate. b: NH_3 molecular condensation (~ 0.45 ML) at 100 K upon an amorphized (by ion etching) c-Si substrate (exposure ~ 1 L). c, d, e, f, h: 10-L NH_3 exposures at increasing substrate temperatures T_s. g: Difference curve between exposed (f) and clean (a) spectra (dashed line).

and decrease with increasing substrate temperature T_s in exactly the same way as the XPS line γ. Clearly, the intermediate XPS line γ corresponds to this UPS signature rather similar to that of condensed NH_3 molecules. In particular, it still presents the narrow $1e$ contribution reflecting N—H bonding. This implies adsorption of NH_X species on the first layer at these temperatures rather than nitrogen adsorption from completely dissociated molecules at temperatures as low as 90 K as suggested by Bozso et al.[2] Yet NH_X adsorption does not exclude the possibility of simultaneous hydrogen adsorption, as shown below and as observed in Ref. 2 by thermal desorption spectroscopy and ion scattering spectroscopy, since NH_X coverage is limited to ~0.25 ML (ML denotes monolayer). The exact nature of these RT adsorbed species NH_X ($X = 1$, 2, or 3?) remains an open question which can hardly be solved without other investigations. Considering the relevant XPS data, i.e., line γ at 398.5 eV, intermediate between the molecular (400.0-eV) and nitride (397.4-eV) lines, the presence of dissociated species ($X < 3$) is probable. This unsettled point is more largely discussed in previous publications[3,4] devoted to adsorption on Si(111)-(7×7) and a-Si surfaces, where similar UPS and XPS features were observed. At any rate, for NH_3 interacting with metals many authors have interpreted their observations in terms of NH_2 or NH fragment adsorption.[6-8]

For T_s near 550 K the UPS features as well as the relevant XPS line γ reflecting the adsorbed NH_X species, fade progressively away and new peaks become visible in the spectra at 590 K near 4.2 eV (spectra g and f in Fig. 2 and d and d'' in Fig. 3), 7 eV (spectra f in Fig. 2 and d and d'' in Fig. 3), and 11 eV (spectrum g in Fig. 2). This signature corresponds to the first thermal nitridation stage. On further NH_3 adsorption (spectrum h in Fig. 2) these peaks become progressively more intense and shift towards three features at higher BE's (4.8, 7.5, and 12 eV, labeled A, B, C) for the same reasons as previously invoked in the case of the XPS core line β. Our data are in good agreement with the UPS measurements of Kärcher, Ley, and Johnson[9] on thick Si_3Ni_4 layers.

In the intermediate temperature range (550 < T_s < 590 K) a contribution at 5.4 eV (spectra f in Fig. 2 and d in Fig. 3) is particularly visible on the difference spectra (g in Fig. 2 and d'' in Fig. 3). We attribute this structure to the well known Si—H monohydride bonds.[10,11]

Additional interesting information can be deduced from the observation of the He_1 spectra in Fig. 3: The clean surface spectrum (a in Fig. 3) shows the strong surface state S characteristic of the 2×1 reconstruction (see, for example, Ref. 12) resulting from the DB's involved in the well-known dimer structure.[13] At RT as well as at 590 K (spectra c and d in Fig. 3) a 10-L NH_3 exposure removes completely these surface states. Such a surface appears to be quite inert since UPS (spectra c' and d' in Fig. 3) and XPS remain unchanged over more than 24 h under UHV conditions: No contamination could be detected in contrast to the very reactive clean surface which, after only 1 h in the same vacuum (spectrum b in Fig. 3), exhibits strong characteristic features of water adsorption at 6.4 eV.[14] These UPS results confirm the remarkable surface
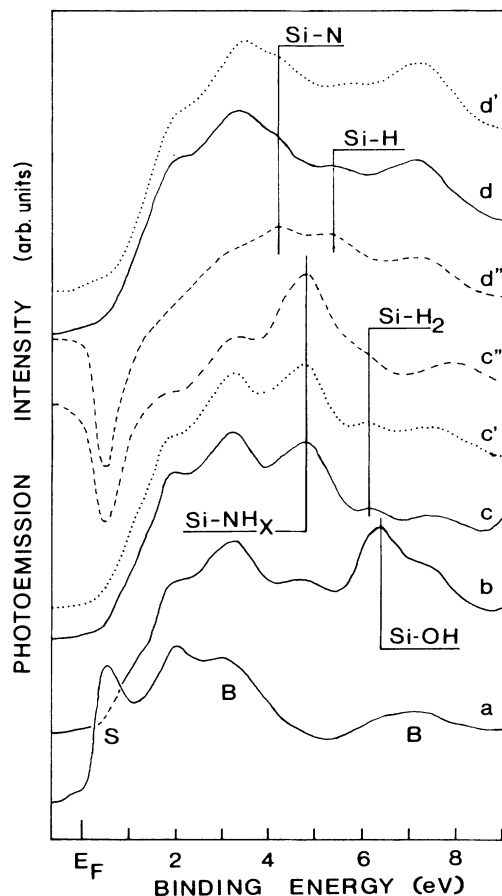

FIG. 3. He I (21.2-eV) photoelectron spectra at emission angle $\theta = 10°$. a: Clean c-Si(100)(2×1) substrate; surface (S) and bulk (B) states. b: The reactive clean surface (a) after exposure to the residual vacuum ($\sim 5 \times 10^{-10}$ mbar) during 1h. All other spectra are from surfaces exposed to 10 L of NH_3. c, c', c'': At RT. d, d', d'': At 590 K. c, d: Full lines: spectra taken immediately after NH_3 exposure. $c'd'$: Dotted lines; spectra taken after a 24-h delay under high vacuum conditions. $c''d''$: Dashed lines; difference curves between exposed c, d, respectively, and clean a spectra.

passivation resulting from such NH_3 exposures against all subsequent interactions as also emphasized by Boszo et al.[2]

At RT the weak contribution (spectra c and c'' in Fig. 3) at 6.2 eV indicates the presence of a SiH_2 dihydride phase[15,16] brought about by dissociative adsorption of the NH_X species. Thus, at RT, passivation results from the simultaneous adsorption of NH_X species and hydrogen in the dihydride phase. At higher temperature near 590 K, the monohydride phase replaces the dihydride one. Such behavior is usually observed upon atomic hydrogenation of Si(100) surfaces.[14,15,17] Simultaneously, atomic nitrogen adsorption resulting from NH_X dissociation can be detected. Therefore, the NH_3 adsorption model on Si(100) is probably much more complex than the uniform hydrogen DB passivation model proposed in Ref. 2. The intensity of the UPS features due to hydrogen bonding are apparently too weak to account for complete surface passivation. Yet

we do not question the partial hydrogen contribution to the DB saturation.

Moreover, our results unambiguously prove that nitrogen in the form γ adsorbed at RT and—*a fortiori*—at 90 K in Bozso's experiment cannot be in a nitride environment.

IV. DISCUSSION

What can be learned from such data on the initial adsorption stages of NH_3 about the nitride layer growth activated by electron beam as observed at RT in Ref. 1 or at 90 K in Ref. 2? According to Glachant et al.,[1] the nitridation would be rate limited by the dissociation of NH_3 on the Si surface possible at high temperature only. The electron beam would enhance this NH_3 dissociation at low T_s. In opposition to Glachant, Bozso et al.[2] assert that NH_3 dissociation on the Si(100) surface is already complete at 90 K owing to the high DB surface reactivity. But at these low T_s, further reaction should be blocked by DB saturation with hydrogen coming from the dissociation: In this case the electron beam is supposed to activate the reaction by H desorption.

Our results suggest an intermediate point of view between these two limiting pictures. In agreement with Glachant et al.,[1] our XPS line γ and UPS spectra reflect still NH molecular orbitals at RT. This proves that the dissociation is not complete at RT. Actually, the presence of weak Si-H features [as well as Si(111) as on Si(100) surfaces] reveals partial dissociation and coadsorption of both NH_X radicals and atomic H. The resulting DB saturation prevents any further surface NH_3 chemisorption. Above 550 K, thermal NH_3 dissociation becomes complete. Yet the sticking remains low (spectrum e in Fig. 1), probably because of the H adsorption. It is only above 700 K that thermal desorption of the monohydride phase occurs and nitridation begins to grow rapidly as can be seen in spectra f and g in Fig. 1, in accordance, in that case, with statements of Bozso et al. But in order to explain the very interesting low T_s, electron beam enhanced nitridation experiments reported by these authors, we suggest that electron irradiation works in assisting both H desorption *and* dissociation of the NH_X coadsorbed radicals at low T_s.

This point of view agrees better with the conclusion arrived at by Glachant et al.,[1] although they did not observe the hydrogen by Auger. Besides, Si—NH_X bonds are not only sensitive to electron beams but also to ion beams. In spectra b and b' in Fig. 1, we report spectra corresponding, respectively, to a surface initially exposed to 10 L of NH_3, and subsequently Ar^+-ion beam bombarded for 15 sec at 2 keV. As shown in spectrum b' in Fig. 1 by the N_{1s} BE shift, ion bombardment destroys the NH_X species and favors the formation of nitride configuration. We had already reported on the same nitrogen configuration changes for amorphous a-Si N_X: H films upon ion-beam etching.[18] Particularly in such films, the NH_X species cannot be observed after usual ion cleaning treatments. Possibly Bozso's ion scattering spectroscopy experiments did not reveal the NH_X species at low T_s, because of an ion-beam artifact, breaking the N—H bonds and leading to nitride environments. Actually, even without invoking this ion-beam effect or considering nitrogen in hypothetical subsurface sites, the observed decrease of the nitrogen contribution in ion scattering spectroscopy after desorption of the molecular species can be accounted for by the rather low coverage (~ 0.25 ML) of chemisorbed NH_X species.

Our results show that while hydrogen DB passivation may be the basic limiting mechanism of thermal nitridation in the 550–700-K temperature range, this is certainly not the case below RT, where adsorption of NH_X species plays a prominent part. Clearly, these statements are not in contradiction with the electron beam assisted nitridation at low T_s as observed in Refs. 1 and 2.

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