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High-resolution electron-energy-loss study of NH_3 adsorption on Si(111)2×1 at room temperature

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We have studied the adsorption of ammonia on Si(111) using surface vibrational spectroscopy and photoemission spectroscopy. The results show that NH_3 is adsorbed primarily as a nondissociated molecule at room temperature. These findings are in contrast with recent results on Si(100), which suggest that a large fraction of the adsorbed ammonia molecules dissociates.

The adsorption of NH_3 on Si is of fundamental and technological interest. In fact, nitridation processes could be important for applications in semiconductor device fabrication and, in particular, NH_3 can be used as a nitridant for producing insulating films of Si_3N_4. A recent Letter by Boszo and Avouris presented experimental evidence that a large fraction of the adsorbed ammonia molecules dissociates on the (100) surface of silicon.[1] The general interest in this process was enhanced by the discovery that soft x rays stimulate the nitridation of silicon.[2]

We used high-resolution electron-energy-loss spectroscopy (HREELS) and x-ray photoemission spectroscopy (XPS) to investigate the adsorption of ammonia on Si(111) at room temperature. In contrast to the Si(100) results of Ref. 1, we found that the adsorption is primarily molecular. While we did observe HREELS features attributed to dissociation products, their intensity was much weaker than that of the features of nondissociated NH_3. The XPS results are consistent with the conclusion that the adsorption is primarily nondissociative on Si(111).

The experiment was performed in an ultrahigh-vacuum chamber equipped with low-energy electron diffraction (LEED), XPS, and a single-pass electron-energy-loss spectrometer (Leybold-Heraeus model No. 22). The working pressure was typically $(1-2)\times10^{-10}$ Torr except during exposure to NH_3. A liquid-nitrogen trap was used to minimize the partial pressure of residual H_2O, which is highly reactive with the Si(111) surface.[3] The Si crystals (n type, 5 Ω cm) were cleaved *in situ* from a $\langle 2\bar{1}\bar{1}\rangle$ direction by the notch method.

Ammonia was introduced to the chamber through an adjustable leak value. Exposure pressure was monitored with an ion gauge and corrected for the NH_3 ionization probability of 1.3 vs N_2. All spectra reported here were taken at room temperature in the specular direction along $\langle 2\bar{1}\bar{1}\rangle$ with the angle of incidence fixed at 50° to the surface normal. The incident electron energy was 6.3 eV. The full width at half maximum (FWHM) of the quasielastic peak in these spectra was typically 16 meV.

We discuss HREELS curves which represent three sets of NH_3 exposures performed on individual Si(111) cleavage surfaces. The single-domain 2×1 reconstruction was verified by LEED for each clean surface. Because of the risk of promoting ammonia dissociation with the LEED beam (50–100 eV), the surfaces used for the HREELS data shown here were not monitored with LEED after each exposure. Using other cleaves, however, it was found that the quenching of the silicon surface phonon by ammonia adsorption corresponded to the fading of the half-order spots. A surface saturated with adsorbed NH_3 has a 1×1 LEED pattern, indicating that the π-bonded chain structure of the clean surface[4] is disrupted by the adsorbate.

Figure 1 shows the results of a set of five successive

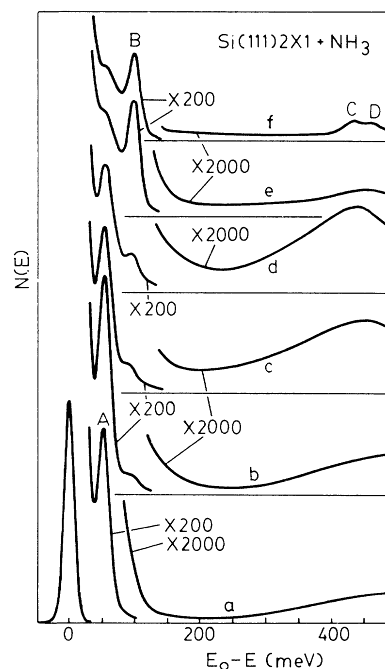

FIG. 1. HREELS taken on a clean, cleaved silicon (111) surface (curve a), and on the same surface after subsequent exposures to ammonia. The exposure levels were 0.05, 0.10, 0.15, 0.20, and 0.25 L for curves b–f. The primary electron beam energy was $E_0=6.3$ eV throughout the experiments.

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0.05-L (1 L $=10^{-6}$ Torr sec) exposures of NH_3. Because the spectrometer required retuning after every exposure, the ratio of adsorbate peak heights to the quasielastic peak height does not necessarily scale with the exposure. However, the ratio of adsorbate peaks to the phonon peak should increase in a reasonably uniform manner. On this basis, it appears that the actual dose of NH_3 delivered by the fourth exposure was anomalously large, although all five exposures were performed by raising the pressure to 5×10^{-9} Torr for 10 s.

The clean surface (curve a, Fig. 1) has the surface phonon at 53-meV energy loss, peak A. The onset of surface-excitation loss structure[5] appears at ≈ 300 meV. The exposures (curves b–f, Fig. 1) result in a weakening of the surface loss feature and of the phonon, which is progressively shifted to 56.5-meV energy loss. A peak (B) appears at 96-meV energy loss (curve b, Fig. 1) and is shifted to 98 meV by successive exposures. A feature, peak C, centered at ≈ 430 meV (curves e and f, Fig. 1), is broader than the others and presumably has overlapping components. A distinct peak (D) is resolved at ≈ 455 meV (curve f, Fig. 1).

Figure 2 shows the results of a set of five successive nominal 0.2-L exposures of NH_3. The initial surface (curve a, Fig. 2) exhibits a weak peak (E) at 98 meV. This is attributed to contamination from ammonia in the residual gas. The surface-excitation peak at ≈ 350 meV suggests a high defect density.[5] The surface phonon shifts from 52 meV (curve a, Fig. 2) to 60 meV (curve e, Fig. 2) before becoming too weak to locate (curve f, Fig. 2); it is much stronger (curve b, Fig. 2) than the phonon on the comparably exposed surface (curve e, Fig. 1). New peaks (F and G) at 190 and 255-meV energy loss are barely visible (curve b, Fig. 2); they increase (curves c and d, Fig. 2), but are not significantly larger (curves e and f, Fig. 2), compared to the other features. A peak appears at 420 meV (curves c–f, Fig. 2); it has a shoulder at ≈ 450 meV.

Figure 3 illustrates another set of exposures. Exposure to 20 L of NH_3 (curve b, Fig. 3) quenches the phonon and surface excitation while producing peaks (H, B, F, and G) at $\approx$65-, 96-, 194-, 255-, and 420-meV energy loss. Photoemission spectra taken on this surface with Mg $K\alpha$ radiation show no detectable chemical splitting of the Si $2p$ and N $1s$ core levels into components. This is in contrast to published results for the Si(100) surface,[1] in which some spontaneous nitridation at room temperature was easily observed by XPS. Thus, the Si(111) surface appears less reactive than the Si(100) surface. The low reactivity of Si(111)2×1 vs Si(100) in the adsorption of H, O, and H_2O has been noted previously.[6]

Since soft x rays from a synchrotron-radiation source are known to promote nitridation,[2] we tested the effect of hard-x-ray beams (Mg and Al $K\alpha$) on the ammonia-covered surface. The results are shown (curve c, Fig. 3). Peaks F and G at 194 and 255 meV are significantly reduced with respect to the others. An additional 20-L exposure (curve d, Fig. 3) partly restored the peak strengths. A set of successive NH_3 exposures followed by Al $K\alpha$ x-ray bombardments (for up to 4 h at half maximum source power) failed to promote detectable nitridation.

Figure 4 shows XPS curves taken with Mg $K\alpha$ radiation on a Si(111) surface saturated with ammonia. Saturation was obtained with 1-L exposure. Further exposure did

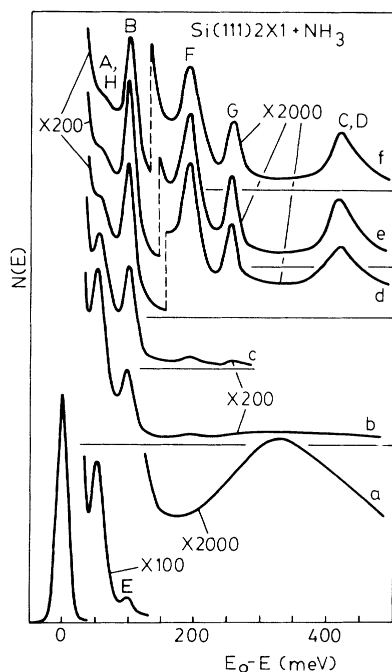

FIG. 2. HREELS curves for a cleaved Si(111) surface (curve a), and for subsequent ammonia exposures, 0.2, 0.4, 0.6, 0.8, and 1.0 L for curves b–f.

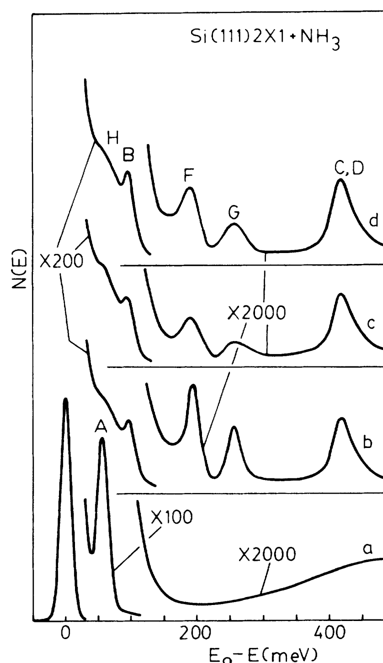

FIG. 3. HREELS curves for a cleaved Si(111) surface (curve a), and for an ammonia exposure of 20 L (curve b). Curve c was taken after bombarding this surface with Mg $K\alpha$ photons, and curve d was taken after further exposure to 20 L.

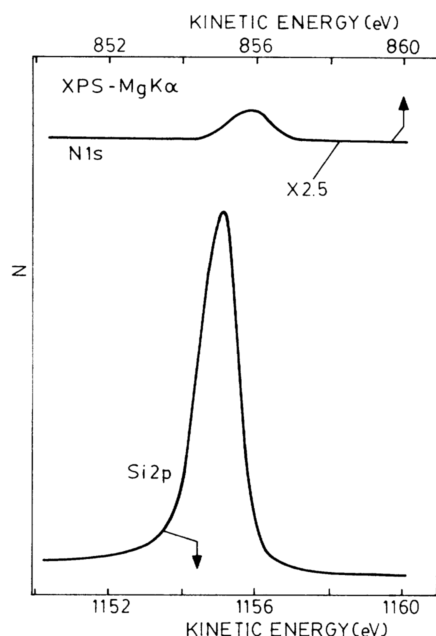

FIG. 4. X-ray photoemission spectra (XPS) taken on cleaved silicon after 1 L exposure to ammonia, using a Mg $K\alpha$ source. The two spectra were displaced vertically for clarity. Further exposure to ammonia did not produce an increase of the N 1*s* signal.

not increase the N 1*s* peak intensity. The Si 2*p* peak has about 25 times the strength of the N 1*s* peak.

The behavior of the surface phonon, peak *A* is of some interest. It has been reported to appear in energy loss as low as 48 meV,[7] although its "normal" position is 57 meV.[8] Its appearance at lower than normal energy loss has been attributed to the presence of multiple small surface domains,[9] cleaved-dependent tilting of the π-bonded chains,[7] and possibly superposition of a normal-energy "chain" mode with a cleave-dependent lower-energy "step" mode.[7]

Multiple small domains can be ruled out in the case. The LEED pattern showed additional half-order spots only when the electron beam was within 50 μm of an edge of the surface. Other HREELS curves (not shown), having contributions from the cleaving notch and side of the sample, consistently show a strong peak near 360-meV energy loss, identified as the C-H stretching mode from hydrocarbon contamination. Since this peak is not detectable in the clean-surface HREELS curves presented here, we infer that the contribution to the signal from the multiple-domain edges of the surface is negligible.

Imaging of the Si(111)2×1 surface by scanning tunneling microscopy[10] shows $\langle 2\bar{1}\bar{1}\rangle$ corrugation asymmetry associated with the structural defects (protrusions, not steps). This asymmetry probably arises from tilting of the π-bonded chains for local strain relief. The lowest-energy phonon position in our study (including spectra not shown in this paper) was 52 meV (curve a, Fig. 2). This surface also had an excitational feature at ≈ 350 meV and high background which were quenched by ammonia adsorption. We suggest that the observed energy of the phonon loss is indirectly cleave dependent in that a high density of protrusion defects produces tilting of π-bonded chains over a relatively large area, with consequent lowering of the phonon energy below its normal value.

In our sequential exposures to ammonia (Figs. 1 and 2), we observe the systematic migration of the phonon to higher energy with increasing NH_3 adsorption. The progressive shift is an entirely different process from the discrete replacement of one loss feature by another in the growth of metal overlayers on the Si(111) surface.[11] There is no evidence for a narrowing of the phonon peak with migration, which casts doubt on the possibility that a step mode contributes to the peak. One would expect the step mode to be quenched more rapidly than the chain mode on the grounds that steps provide the favored sites for molecular adsorption.[8,12]

We now turn to interpretation of the adsorption process itself. Strongly dissociative adsorption of NH_3 on Si(100) has been reported.[1] Previous low-resolution energy-loss and photoemission studies of NH_3 on Si(111)7×7 at room temperature show molecular adsorption with no detectable dissociation.[13,14] However, the sensitivity of these techniques is much worse than HREELS in detecting dissociation products in low concentration. Using HREELS, we find that the adsorption of NH_3 on Si(111)2×1 at room temperature is primarily molecular, but some ammonia does dissociate into NH_2 and H.

The photoemission spectra (Fig. 4) indicate that saturation occurs with approximately one N atom per two surface Si atoms. This can be demonstrated by considering that the mean free path for electrons of the relevant energy in silicon is ≈ 40 Å,[15] and the atomic concentration is 5.0×10^{22} cm^{-3}, so the effective areal atomic concentration of silicon atoms contributing to the signal is 2×10^{16} cm^{-2} or 2 atoms per square angstrom. The (111) surface has one Si atom per parallelogram of area $\sqrt{3}a^2/4$, where $a = 5.43$ Å is the lattice constant. This is 1 atom per 12.8 square angstroms or about $\frac{1}{25}$ the effective concentration giving the Si 2*p* signal. With Mg $K\alpha$ photoemission, the atomic sensitivity factor for N 1*s* is roughly twice what it is for Si 2*p*.[16] Therefore, the XPS data indicate that there is approximately one nitrogen atom per two surface silicon atoms at saturation.

Depending on the type and extent of dissociation, the nitrogen may be in N, NH, NH_2, and NH_3 species. The most prominent adsorbate-induced energy-loss peak (*B*) occurs at 96 to 99 meV. This peak could be attributed either to the symmetric NH_3 deformation or to the Si-N-H bend. If the largest adsorbate peak were due to the latter vibration, indicating strongly dissociative adsorption, then we would also expect to see a large peak (*G*) around 255 meV from the Si-H stretch. In curve f, Fig. 1, however, peak *B* is very intense while peak *G* is not visible. Therefore, we attribute peak *B* to the symmetric NH_3 deformation. It is at significantly lower energy than the corresponding vibration in free ammonia, 116 meV.[17] By contrast, this vibration is shifted to higher energy when NH_3 is adsorbed on metal surfaces.[18–21] A possible explanation for this difference is that bonding of ammonia to Si(111)2×1 differs distinctly from its bonding to metal surfaces.

The broad peak H at $\approx$65-meV energy loss, best seen in Fig. 3, is interpreted as a frustrated translation of the adsorbate normal to the surface. Its low-energy value rules out the possibility that the adsorbed species sit on top of individual substrate atoms. If they did, then the frustrated translation would represent a modified Si-N stretching vibration, whose energy in the free state is 143 meV.[22] It seems likely that the NH_3 molecules occupy hollow sites of C_{3v} symmetry on the (111) surface.

The features C, D in the 420–440-meV energy-loss range are attributed to the symmetric NH_3 stretching mode. This mode is quite sensitive to the strength of the interaction between NH_3 and the surface. Comparing curve b, Fig. 3; curve f, Fig. 2; and curve f, Fig. 1, we see that the height of the 420–440-meV peak changes from surface to surface with respect to that of the deformational peak at 96–99 meV. However, these changes are compensated by modifications of the width, and the areas appear comparable for all surfaces. Since the surface in Fig. 3 had its phonon in the normal position, it probably had the lowest defect density. This surface shows a uniform interaction strength with NH_3, as seen through the narrowness and symmetry of the stretching peak at $\approx$420 meV. The broader peaks in the spectra of the other two surfaces suggest that defects are locally responsible for small changes in the interaction energy of the adsorption.

Peak D at $\approx$455-meV energy loss is interpreted as the result of water contamination. In the study of H_2O adsorption on Si(111)2×1 at room temperature,[6] which is an almost entirely dissociative process, it is found that the loss peak heights for the O-H and Si-H stretching modes are nearly equal throughout the exposures. On the other hand, we find (curves e and f, Fig. 1) that while peak D is clearly visible, the Si-H peak G at $\approx$255 meV is below the level of detection. This suggests that peak D represents the symmetric H_2O stretching mode rather than the O-H stretching mode. Hence the NH_3 coverage, although well below saturation (curve f, Fig. 1), is sufficient to prevent H_2O dissociation, presumably by tying up the active sites where such dissociation occurs.

In our higher coverages (curves c–f, Fig. 2, and curves b–d, Fig. 3), we do observe the Si-H stretch at 255 meV, peak G, and we find that it greatly exceeds peak D at $\approx$455 meV in amplitude at saturation. Thus, the Si-H signal cannot be interpreted as a result of water dissociation. This indicates that some NH_3 dissociates. In our spectra, peak F at 190 to 194 meV is present when and only when the Si-H peak is also present. The height ratio between the peaks is 5:3. We identify peak F with the NH_2 scissor mode. The height of the NH_2 peak at saturation is about $\frac{1}{10}$ that of the NH_3 deformational peak. The fact that the former is not observed (curves e and f, Fig. 1) indicates that significant dissociation of NH_3 does not occur at low coverage.

The x-ray bombardment (curve c, Fig. 3) resulted in a reduction of the NH_2 and Si-H peak heights relative to the others. While it is probable that all species suffered some desorption by this process, it is apparent that NH_2 and H are more easily desorbed than molecular NH_3. Another ammonia exposure after x-ray bombardment (curve d, Fig. 3) partly restored the NH_2 and Si-H peak strengths. This suggests that specific sites are involved in dissociation and that NH_3 molecules, once adsorbed, do not migrate laterally to the dissociation sites. Since molecular NH_3 prevents H_2O from dissociating, it appears that the sites and mechanisms for H_2O and NH_3 dissociation on Si(111)2×1 are different.

In conclusion, our data show that adsorption of NH_3 on Si(111)2×1 is primarily molecular with some dissociation into NH_2 and H. These results differ from those obtained with other surface-sensitive techniques on other silicon surfaces. In particular, they indicate that the amount of ammonia that dissociates at room temperature strongly depends on the crystallographic orientation of the silicon substrate.

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