Local Structure of NH_2 on Si(100)-(2 × 1) and its Effect on the Asymmetry of the Si Surface Dimers

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A scanned-energy mode photoelectron diffraction study of the Si(100)-(2 × 1) surface with adsorbed NH_2 provides quantitative determination of key structural parameters previously only predicted from theoretical calculations. In particular, the N atoms occupy off-atop sites at a dimerized surface Si atom with N-Si bond lengths of 1.73 ± 0.08 Å and bond angle relative to the surface normal of $21° \pm 4°$. The adsorption greatly reduces the Si dimer asymmetry relative to that of the clean surface. [S0031-9007(97)03662-4]

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The interaction of Si surfaces with certain molecular reactants is of considerable interest due to their role in the processing of semiconductor devices. Despite the extensive spectroscopic and theoretical studies of such systems, there remains a dearth of quantitative structural studies on which to base our understanding of the electronic and geometrical structure and the chemical reactivity. One specific example is the interaction of Si(100) with NH_3, of potential interest to surface nitridation. On this surface ammonia is found to adsorb dissociatively even at low temperature (90 K), and at room temperature there is general agreement that electronic and vibrational spectroscopies are consistent with a surface layer comprising coadsorbed NH_2 and H (e.g., [1–6]). An early scanning tunneling microscopy study at room temperature [7] was interpreted in terms of subsurface atomic N and adsorbed H, but the general consensus concerning the probable structure is now of NH_2 and H species adsorbed at opposite ends of the Si dimers present on the clean surface. This consensus, however, is based only on indirect evidence and theoretical total energy calculations [8,9]. Here we present the results of a scanned-energy mode photoelectron diffraction (PhD) [10] investigation of this system prepared under conditions known to produce coadsorbed NH_2 and H which provides quantitative information not only on the N adsorption geometry, but also on the modification which the adsorbates induce in the asymmetric Si dimers of the clean surface structure. The results are in excellent agreement with one of the theoretically deduced structures and help to clarify controversies in the literature as to the role of the local structure on electronic probes of the surface and the degree of ionicity in the surface dimers.

The PhD technique [10] is based on the analysis of the coherent interference of the directly emitted component of an adsorbate core level photoelectron wave field with components of the same wave field elastically backscattered from surrounding substrate atoms. The intensity of emission detected in a specific direction is modulated as the energy and thus wavelength of the photoelectrons is varied, causing the backscattering pathways to be alternately constructive and destructive. A first-order structure analysis can be obtained from a set of such PhD spectra recorded in different emission angles by a simple Fourier-transform method [11,12], while full quantitative analysis is then undertaken using structural iteration through a comparison of the experimental spectra with the results of multiple scattering simulations [13,14] for a series of trial structures. We have previously described this methodology in detailed quantitative determinations of more than 30 adsorbate structures on metal surface (see [10] and references therein). In the present case N 1*s* PhD spectra were recorded at polar emission angles from 0°, 5°, 10°, 20°, 30°, and 40° in a ⟨110⟩ azimuth and at 10°, 20°, and 30° in a ⟨100⟩ azimuth, each in the kinetic energy range 45–420 eV, and this set of 9 PhD spectra, covering a total energy range of 3375 eV (comparable to the best LEED analyses), was used in the structure determination. The experiments were conducted at the BESSY synchrotron radiation facility in Berlin using the HE-TGM1 beam line and end station described elsewhere [15]. The Si(100) sample was cleaned by cycles of argon ion bombardment and heating to 1500 K until judged to be clean and well ordered on the basis of a sharp (2 × 1) LEED (low energy electron diffraction) pattern and both Auger electron and soft-x-ray photoelectron spectroscopies. The surface was then dosed with 1 L NH_3 at room temperature. As reported in the literature, the (2 × 1) LEED pattern remained after this treatment. The sample was then cooled to 200 K to reduce the influence of thermal vibrations on the PhD data.

Fourier transform intensity contour maps obtained from the PhD spectra recorded in the two principle azimuths indicated that the N atoms occupy sites approximately atop surface Si atoms. Full multiple scattering calculations (see below) confirm but refine this conclusion. In particular, the optimum fit structure has a Si-N bond angle relative to the surface normal of 21° ± 4°; the length of this nearest neighbor bond is 1.73 ± 0.08 Å. This geometry is shown schematically in Fig. 1.

Although this local adsorption site determination is already an important new piece of information, a further key issue is the extent of modification of the outermost substrate atomic layers. In the case of the Si(100)-(2 × 1) clean surface the structure of these layers differs significantly from that of the underlying bulk phase, and although the retention of the (2 × 1) diffraction pattern on reaction with NH_3 shows that there is no modification of the two-dimensional periodicity, we would expect some adsorbate-induced modification of the local atomic positions. In particular, on Si(100)-(2 × 1) it has long been recognized that the key structural element of the surface is Si dimers, but we seek to quantify the influence of the adsorbed NH_3 reaction products on the degree of geometrical asymmetry of these dimers.

Even on clean Si(100)-(2 × 1) the existence or extent of Si dimer asymmetry has been the subject of very considerable controversy, but it is now clear that the dimers in this structural phase are asymmetric. One problem in determining this asymmetry is that at room temperature in the (2 × 1) phase there is no long-range ordering of the asymmetries, but the dimers are dynamically “flipping” between the two inequivalent orientations so that “up” and “down” Si atoms at the two ends of the dimer change their up or down assignments on a time scale estimated to be 10^{-9} s [16]. This accounts for the fact that while photoemission, which samples on a much shorter time scale, shows inequivalent Si $2p$ binding energies associated with the up and down atoms (e.g., [17–23]), room temperature scanning tunneling microscopy (STM) samples on a longer time scale and shows no such asymmetries [24,25]. STM conducted at low temperatures, when the flipping is “frozen,” confirms this picture [26]. Recent theoretical total energy calculations [27,28] and experiments which are insensitive to long-range ordering (notably x-ray reflectivity [29] and photoelectron diffraction [30]) all indicate that the Si surface dimer axis is tilted by between 15° and 20° to the surface.

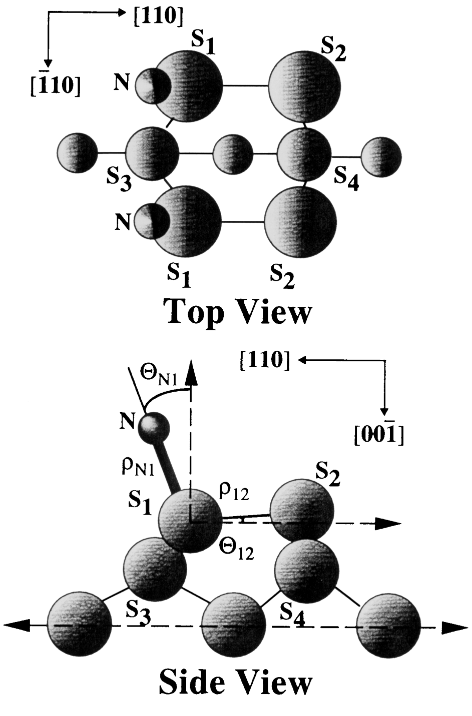

FIG. 1. Schematic diagram showing the optimized structural parameters for the N atom in adsorbed NH_2 on Si(100) obtained from fitting the N 1s photoelectron diffraction data by multiple scattering calculations.

To establish the extent of dimer asymmetry in the presence of the adsorbed reaction products (as well as the exact NH_2 adsorption site) we have carried out a structural optimization using full multiple scattering simulations of our complete photoelectron diffraction data set. This was conducted over a wide range of structural parameter space with the aid of a “linear” approximation method [14] and exact calculations coupled with a Newton-Gauss optimization procedure. The optimization involved minimization of a reliability factor (R factor) [31] based on a sum of square deviations between theory and experiment normalized in a similar fashion to the Pendry R factor [32] used in LEED. The precision was estimated using a variance also computed as described by Pendry [32] which takes into account the sensitivity of the fits to each structural parameter, the quality of the best fit, and the size of the experimental database. Noise in the experimental data also automatically influences the variance and thus the estimated precision. Our search explored the influence of both different local N adsorption geometries and of different surface geometries of the Si substrate itself. One potential complication of surface structure determination for semiconductors is the likelihood that many inequivalent atoms in the outermost few layers will suffer some positional changes relative to the extended bulk structure, because in a covalently bonded network local distortions can propagate over several interatomic spacings. This is a problem for LEED as failure to account for small subsurface distortions can lead to errors in the optimal positions of surface atoms. Because PhD is a far more local structural technique, this problem is much less significant. Tests showed no significant sensitivity to any reasonable distortions of the Si substrate below the outermost layer (the layer of dimers). We therefore concentrated on structural searches constrained to movements of the N emitter and Si surface dimer atoms relative to a subsurface which has the bulk-terminated structure. The comparison between theory and experiment of the PhD spectra for the best-fit structure is shown in Fig. 2. The good fit is reflected by the low R factor value of 0.165.

There are two main structural "signatures" of Si dimer asymmetry. One of these is the Si-Si dimer bond angle relative to the surface. To determine this angle one must locate the Si atom (S_2, Fig. 1) of the dimer not bonded to the NH_2 species, but because there is only one such atom, the favored N-S_2 backscattering geometry is far from the surface normal, and the calculations must average over four inequivalent structural domains, the sensitivity of our N 1s PhD spectra to this atom location is low. The bond angle is found to be 8° ± 8°, a range including both the asymmetric dimers of the clean surface and a perfectly symmetric dimer. The second characteristic which distinguishes asymmetric and symmetric dimers is the lateral position of the dimer atoms relative to the substrate (asymmetry leads to a lateral displacement of the center of the bond along the bond axis, as seen schematically in Fig. 1) and the height of each of the dimer atoms above the second Si layer. In this case the PhD data are much more incisive, being sensitive to the location of the N emitter and nearest neighbor Si atom (S_1 in Fig. 1) relative to the substrate (Fig. 3 shows the R factor variation with respect to the relevant structural parameters defining these two locations). Convenient parameters to define the location of this S_1 Si atom are x_{13} and z_{13}, the coordinates of this atom relative to a second layer Si atom (S_3 in Fig. 1) in the [110] and [001] directions, respectively. For a bulk-terminated solid these parameters would be 0.00 and 1.36 Å. The experimental values are 0.50 ± 0.25 and 1.12 ± 0.06 Å. Typical values for a clean surface asymmetric dimer, taken from a recent theoretical total energy calculation [27], are 1.04 and 0.69 Å if S_1 is a down atom and 0.61 and 1.39 Å if S_1 is an up atom. Evidently neither of these pairs of values fits the experimental result. By contrast, the same parameters for a calculated (hypothetical) symmetric dimer on clean Si(100) have been cited as 0.80 and 1.03 Å [33], much closer to the experimental values. These theoretical values are in even better agreement if we recognize that the Si-Si dimer bond length can be expected to increase relative to its value on the clean surface (2.24 Å) as a consequence of bonding NH_2 to one end and H to the other to about 2.42 Å [9]. Retaining substrate atom positions and the Si first-to-second layer bond lengths for a symmetric dimer of this length yields x_{13} and z_{13} values of 0.71 and 1.09 Å. Indeed, we may also compare our experimental values with these coordinates from the slab calculations of the adsorption structure [9] (0.60 and 1.19 Å) and find excellent agreement; the corresponding Si-Si dimer bond angle is 2.2°. It is clear, therefore, that our data support an essentially symmetric dimer geometry after adsorption and are inconsistent with the retention of the strong asymmetry of the clean surface.

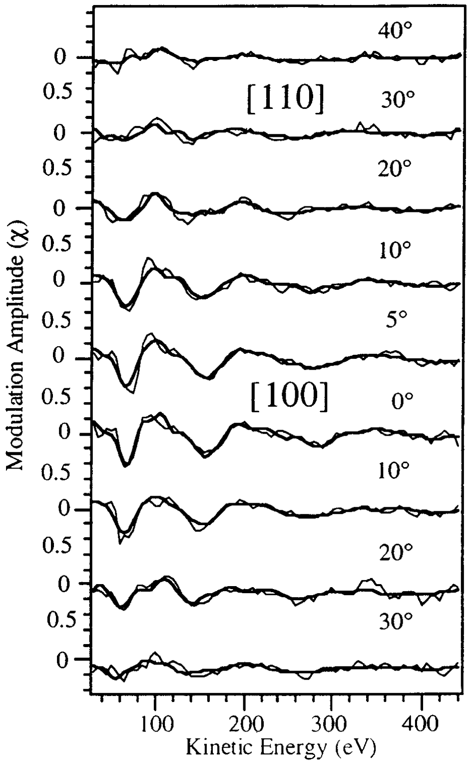

FIG. 2. Comparison of experimental N 1s photoelectron diffraction spectra (thinner line showing noise) from NH_2 on Si(100) with the results of multiple scattering calculations (bold line) for the best-fit structure (see Fig. 1 and text).

The local Si-N geometry found in our study is also well simulated by the published slab calculation; the experimental Si-N bond angle relative to the surface normal and bond length are 21° ± 4° and 1.73 ± 0.08 Å while the theoretical values are 22.8° and 1.707 Å, respectively. A theoretical cluster calculation gave a similar bond angle (25°) but gave a bond length (2.04 Å)

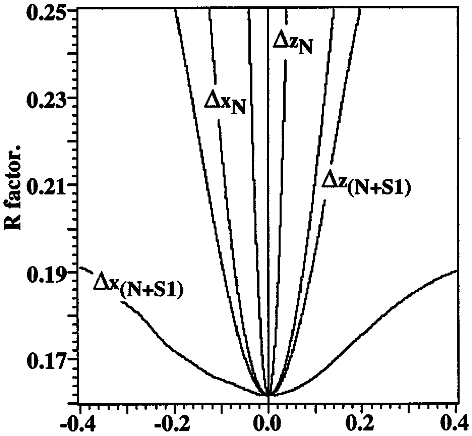

FIG. 3. Dependence of the R factor on changes in the position of the N emitter (z_N and x_N) relative to all other atoms, and on the position of the $S1$ atom when moved together with the N emitter relative to the substrate. These curves are the basis of the precision estimates quoted in the text. Note that displacing $S1$ alone shows stronger variation due to changes in the N-$S1$ relative position to which the data are most sensitive.

which lies well outside the estimated errors of the experimental determination. Other estimates of the Si-N bond angle to be found in the published literature are somewhat speculative in their basis; our value is consistent with the estimate of 20° made by Fujisawa *et al.* [5] but not with the 35° estimated by Dresser *et al.* [6].

There is no published direct experimental information on the Si dimer asymmetry after NH_3 reaction (or, indeed, after any other molecular reaction). One piece of indirect information concerns measurements of Si $2p$ photoemission core level binding energy shifts. On the clean surface theoretical calculations including both initial and final state effects [22] do identify distinct binding-energy shifts for the up and down Si atoms of the asymmetric dimers, and confirm that there is significant charge transfer ("ionicity") between the dimer atoms. Changes in these experimental binding energies following NH_2/H coadsorption have been reported and can be interpreted in terms of a greater covalency and thus reduced symmetry [34]. Such an interpretation, however, neglects the role of final state effects which have been shown to be important for the clean surface [22]. In the absence of full calculations including these effects we note that even though our structural results do show the dimer to be essentially (geometrically) symmetric in the presence of NH_2 and H, this does not necessarily mean that the charge transfer is lost, because the dimer is now chemically asymmetric. An interesting analog of the situation is that of the (110) surfaces of III-V semiconductor surfaces on which a bond rotation of III-V atom pairs (parallel to the surface within the bulk) occurs. At least for the case of InP reaction with H_2S to produce coadsorbed SH and H at the cation and anion sites, respectively, adsorption leads to a restoration of the outermost substrate layer atoms to essentially bulk-terminated sites [35]. In this system, of course, in which the analog of the Si dimer is a pair of inequivalent atoms, it is likely that the local ionicity remains despite the removal of the bond rotation.

In summary, we have used scanned-energy mode photoelectron diffraction to provide the first quantitative determination of a molecular adsorbate geometry on a technically important Si surface, specifically coadsorbed NH_2 and H on Si(100) resulting from interaction with NH_3. The results confirm prior speculation concerning the adsorption sites, and provide quantitative structural parameters in good agreement with one of the previous theoretical calculations on this system. The results not only provide quantitative values for the Si-N bond length and bond angle, but also show that the adsorbates substantially reduce, or possible remove, the geometrical asymmetry of the Si dimers present on the clean surface.

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