

Scanning tunneling microscopy of atomic structure, electronic properties, and surface chemical reactions

N. S. Maslova and V. I. Panov

M. V. Lomonosov State University, Moscow
Usp. Fiz. Nauk **157**, 185–195 (January 1989)

This paper is a review of the application of scanning tunneling microscopy (STM) to the study of the electronic properties of clean surfaces, the changes in the electronic properties upon adsorption and surface chemical reactions, and the role that the electronic properties of a surface play in the formation of chemical bonds during reactions and in the formation of surface structures. The effect of the local density of electron states on the STM image of atoms of various elements is shown. A description is given of the electronic properties and the atomic structure of the reconstructed Si(111)-(7×7) surface. The example of the chemical reaction of NH₃ with the Si(111)-(7×7) surface is used to show that the reactivity of various atoms is directly related to the presence of localized dangling bonds.

CONTENTS

1. Introduction	93
2. Adsorption of oxygen on the GaAs(110) surface	93
3. The reconstruction Si(111)-(7×7) surface	95
4. Electronic structure of the reconstructed Si(111)-(7×7) surface	96
5. Chemical reactions on the Si(111)-(7×7) surface	97
References	99

1. Introduction. Recent years have seen the intensive development of a new method of studying surfaces, a method that makes it possible to study surface microtopography and electronic properties with spatial resolution at the atomic level.¹ The method is based on the phenomenon of electron tunneling between two electrodes, one of which is the surface to be studied and the other is a probe tip of small radius. The extremely high resolution that is realized in this method is due to the exponential dependence of the tunneling current on the barrier parameters—its width, which is determined by the space between the electrodes, and its height, which is related to the work functions of the materials comprising the tip and the surface.

The use of the scanning tunneling microscopy (STM) method allows a detailed investigation of the character of the electronic properties of clean surfaces and the changes in the electronic properties that occur during adsorption or catalysis, and it makes it possible to determine the nature of these changes during surface chemical reactions and thereby provides a means of solving fundamental problems of the role of the electronic properties in the formation of chemical bonds and the formation of surface structure.

2. Adsorption of oxygen on the GaAs(110) surface. The method of STM has been used for the investigation of the adsorption of oxygen atoms on the *n*-type GaAs(110) surface.² The doping level of the GaAs by Si atoms was 10¹⁸ cm⁻³.

The experiments showed that the image of the adsorbed oxygen (O) depends strongly on the voltage V_s applied to the sample, and especially on the sign of V_s .

If a negative voltage is applied to the sample, the atoms show up as protrusions, and for a positive voltage they appear as holes (Fig. 1). This appearance comes about because

the tunneling current at a particular position of the probe tip of the tunneling microscope depends both on the surface relief and on the energy structure of the local density of states.

$$I \sim \frac{2\pi e}{h} \int dE D(E, V_s, d(\mathbf{r}_0)) v_t(E) v_s(E, \mathbf{r}_0) \times [f(E) - f(E + eV_s)] \sim \frac{2\pi e}{h} D(E_F, d(\mathbf{r}_0)) v_t(E_F) \int_{E_F - eV_s}^{E_F} dE v_s(E, \mathbf{r}_0);$$

where v_t is the density of states of the tip, v_s is the density of states of the sample surface, and $d(\mathbf{r}_0)$ is the distance of the surface from the tip if the tip is at the point \mathbf{r}_0 .

If the scanning tunneling microscope is operated with

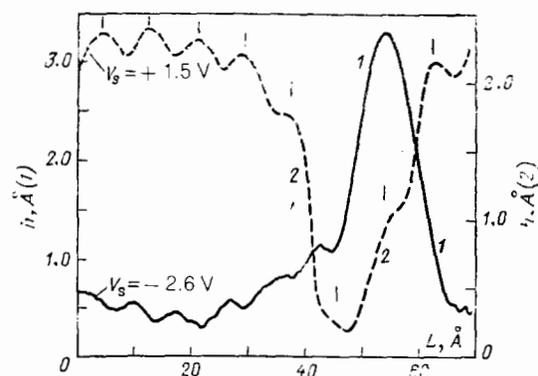


FIG. 1. STM image of oxygen adsorbed on the surface of *n*-type GaAs, taken for various sample voltages.

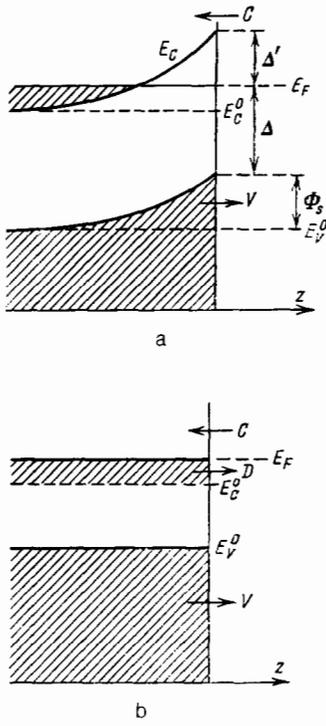


FIG. 2. Band structure near the surface of GaAs. (a) with adsorbed oxygen (the lower curve is E_V) and (b) without adsorbed oxygen.

the tunneling current held constant, then a change in the position of the tip, and consequently in the STM image that is obtained, is determined both by the surface relief and by the change in the density of states over the sample. The energy dependence of the local density of states on the sample surface determines at what voltages V_s the image of adsorbed atoms of a particular element appears.

Oxygen has 2p states which lie below the Fermi level E_F for GaAs. Consequently, the O atom adsorbed on *n*-type semiconductors has a negative charge. The excess negative charge that appears on the surface causes the energy bands to bend near the surface, and a gap appears in the density of states spectrum immediately above the Fermi level (Fig. 2a). It might be thought that the size of the region in which the band bending is important should be of the order of the radius of the 2p shell of the O atom on GaAs. In fact, the following happens. The region in which band bending is important is determined by the range of the potential created by the negative charge concentrated around the adsorbed O; i.e., the Debye screening length:

$$L_D = \left(\frac{2\pi e^2 n}{\epsilon k T} \frac{\Phi_{-1/2}(E_F/kT)}{\Phi_{1/2}(E_F/kT)} \right)^{-1/2},$$

where $\Phi_m(E_F/kT)$ is the Fermi integral of order m .

From this relation we find, for a silicon concentration of $\sim 10^{18} \text{ cm}^{-3}$, the result $L_D \sim 56 \text{ \AA}$. This conclusion is supported by the O-atom STM images, which have a characteristic transverse dimension $L \sim 50 \text{ \AA}$ (see Fig. 1).

Confirmation of the band bending that results from the absorption of oxygen atoms comes also from a comparison of the I-V characteristics of a tunneling junction for a clean surface with that for a surface with adsorbed oxygen, measured in Ref. 2 (Fig. 3).

For a clean surface with small negative voltages applied to the sample, the electrons tunnel out of the filled states of

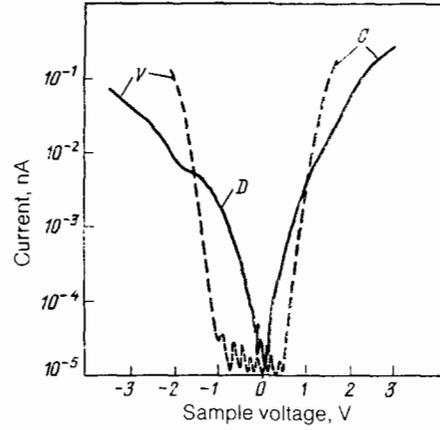


FIG. 3. I-V characteristics of a tunneling junction for the clean GaAs surface (solid line) and for the GaAs surface with adsorbed oxygen (dashed curve). The notation C, D, and V refers to different components of the tunneling current.

the conduction band of the sample (in Fig. 2b, D is this component of the tunneling current). Here the Fermi level lies in the conduction band because of the doping. If $|eV_s| > E_F - E_V$, then electrons from the valence band also take part in the tunneling (V is that component of the tunneling current). For a clean surface, the condition

$$|eV_s| = E_F - E_V, \quad V_s < 0$$

corresponds to the point at which the slope of the I-V characteristic changes.

For positive voltages on the sample the current is determined by the tunneling of electrons into empty states of the conduction band above the Fermi level (the C-component of the current).

With oxygen adsorbed on the surface the bands are bent (see Fig. 2a). If $V_s < 0$ and $|eV_s| < \Delta$, then there will be no tunneling current, since the Fermi level near the surface lies in the band gap on account of the band bending. For

$$|eV_s| = \Delta,$$

where $\Delta = E_F - E_V + \Phi_s$ (Φ_s is the characteristic amount of a bending) a current arises because of tunneling of valence band electrons (the V component of the current). In this case the adsorbate atoms show up very well in the STM image.

If a positive voltage $V_s > 0$ is applied to the sample with

$$|eV_s| < \Delta',$$

then there will be no tunneling current because the band bending causes a gap in the density of states immediately above E_F .

For

$$|eV_s| \geq \Delta',$$

the electrons tunnel into the conduction band of the sample, into unfilled states lying in the range $\sim eV_s$ above the Fermi level. The effective number of such states, however, is smaller than in the case of the unbent bands of the clean surface.

For $V_s > 0$ with

$$|eV_s| > \Delta',$$

the decrease in the tunneling current due to the change in the density of states resulting from the band bending in the neighborhood of the adsorbed atom can compensate the increase in the current due to the increase in the density of states created by the O atom on the real surface. To maintain I constant, therefore, the tip comes closer to the surface in the neighborhood of the adsorbed atom, so that the adsorbed O atoms show up in the STM image of the surface as depressions, and not as protrusions. This appearance comes about because of the change in the local density of states in the neighborhood of the adsorbed O atom, which on GaAs (n-type) has a negative charge.

In p-type GaAs the situation is different. The adsorbed oxygen is electrically neutral, and therefore there is no band bending. This picture is supported by the results reported in Ref. 3, where the adsorbed O atoms always appear as protrusions. The width of the image of the adsorbed O atom is 5–10 Å, which indicates the absence of Debye screening. This simple example of oxygen adsorption makes evident what an important role the local density of states plays in the investigation of adsorption by scanning tunneling microscopy.

3. The reconstruction Si(111)-(7×7) surface. The reconstruction of the Si(111)-(7×7) surface has for a long time attracted the attention of theorists and experimentalists. This interest stems from a number of considerations. One is that theoretical and experimental investigations of complicated unit cells such as the Si(111)-(7×7) which form on a clean solid surface, promote an understanding of the mechanism of their formation. Another is that the reduction in the dimensions of microelectronics elements, to the point where the role of the surface becomes dominant, requires an exact knowledge of the atomic and electronic structure of the surface.

The complexity of the Si(111)-(7×7) cell (which contains 102 atoms) and the absence of experimental methods that would permit a detailed study of the atomic and electronic structure within the cell itself, for a long time left a considerable degree of arbitrariness in the choice of theoretical model that would adequately describe the reconstruction of Si(111)-(7×7).

The invention of the STM method made it possible to study quantitatively, with a longitudinal resolution of ~ 1 Å,

the structural and electronic properties of the surface and thereby, from among the large number of theoretical models of the reconstruction of Si(111)-(7×7), afforded a possible choice of the one that corresponded most closely with experiment.

Figure 4, a-e shows STM images calculated for the most important theoretical models purporting to describe correctly the reconstruction of the Si(111)-(7×7) surface. The calculations were carried out by the method of superposition of atomic charge density.⁴ According to this model, to each atom in the crystal there corresponds an exponentially decaying spherically symmetric density of charge. The charge density at an arbitrary point can be found by summing the charge densities from all the atoms located sufficiently close to this point. This method, however, does not take into account the contribution of surface states to the structure of the electron density. Nonetheless, the results obtained in this way for the charge density distribution near the surface corresponds quite well with the image observed in the STM provided the applied voltage is chosen so that the surface states do not contribute significantly to the tunneling current.

In Fig. 4, e and f, we show for comparison STM images of the relief of the Si(111)-(7×7) surface, obtained experimentally with a 2-volt potential difference between the probe tip and the surface, with the positive potential on the sample. The solid lines in the lower part of the figures show the relief contour along the long and short diagonals of the 7×7 unit cell, as calculated from the models of Refs. 5–9. The dashed lines show the experimental curve. It follows from these results that the theoretical model that corresponds most closely to experiment is the one by Takayanagi (see Ref. 5).

The existing difference between the experimental and the theoretical curves near the corner holes is most likely due to the effect of the finite radius of the probe tip, since a tip of finite radius cannot drop very deep into the small-diameter corner hole. Nonetheless the extremely high accuracy with which the theoretically obtained image coincides with the experimental image allows us to conclude that it is this particular model of the Si(111)-(7×7) surface reconstruction that is the correct one.

According to the model of Takayanagi,⁵ the recon-

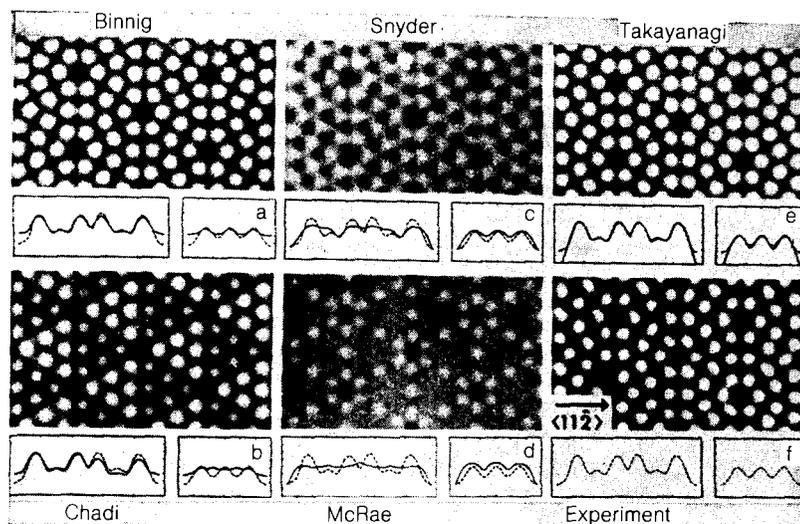


FIG. 4. STM images of the Si(111)-(7×7) surface, calculated for various theoretical models. The models are from: a) Ref. 6; b) Ref. 7; c) Ref. 8; d) Ref. 9; e) Ref. 5; f) experimental curve.

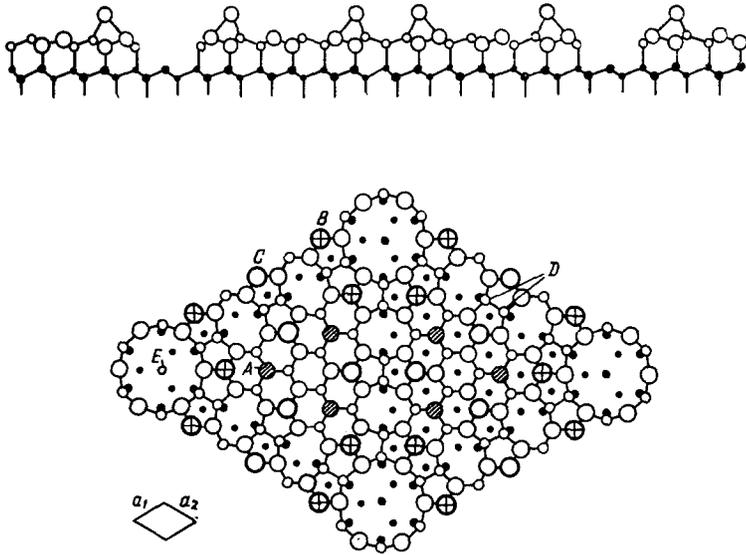


FIG. 5. Model of the reconstructed Si(111)-(7×7) surface (Ref. 5). Adatoms: B (corner) and C (center); A—rest atom; D—dimer; E—corner vacancy.

reconstructed Si(111)-(7×7) surface is arranged in the following way (Fig. 5).

The topmost layer of the unit cell contains 12 adatoms, each of which is bonded to three atoms of the (1×1) first surface layer, and each of the latter in turn forms a bond with the underlying dimer layer. As a result, the adatoms have a single dangling bond, while the atoms of the first surface layer, directly bonded to the adatoms, do not have dangling bonds.

The six atoms of the first surface layer (rest atoms), not directly bonded to the adatoms, also have dangling bonds.

Corner atoms of the (7×7) unit cells are missing from the first surface layer and, as a consequence, a corner vacancy with a dangling bond is formed.

A characteristic feature of the Takayanagi model is the presence of dimer chains on the sides and along the small diagonal of the unit cell. Thus, in each unit cell of the reconstructed Si(111)-(7×7) surface there are 19 electrons that form dangling bonds which are created by 12 adatoms, 6 rest atoms, and a single corner vacancy.

4. Electronic structure of the reconstructed Si(111)-(7×7) surface. The scanning tunneling microscope also makes it possible to study the electronic surface states of the Si(111)-(7×7) surface. A comparison of the images of the same region of the surface, obtained with various voltages V_s and values of the quantity $(dI/dV_s)I/V_s$, which is proportional to the local density of states, measured at various points of the surface with atomic resolution, permits a determination of the electron structure of the Si(111)-(7×7) surface.

According to the results of Refs. 10 and 11, one can distinguish three types of filled or partially filled electron states having various energies.

a) States which have a maximum density in the vicinity of the adatoms and form a partially filled band of surface states corresponding to dangling bonds on the adatoms. The characteristic energy of these states is -0.35 to -0.45 eV.

b) States that are localized primarily on the rest atoms and have an energy of about -0.8 eV as reckoned from the Fermi energy E_F . These are dangling-bond states on the rest atoms, and are essentially completely filled. There are two dangling electrons on each rest atom.

c) Filled electron states, which form Si-Si valence bonds (back bonds) and have an energy of -1.7 eV.

For these states the maximum electron density is located between the adatoms.

Figure 6 shows images of the Si surface with various voltages applied to the sample.¹⁰

When negative voltages are applied to the sample the current is composed of electrons tunneling from the filled states of the sample. The image of the surface for $V_s = -0.35$ eV allows us to trace the structure of the electron density on the 12 adatoms (Fig. 6a). The density of filled states on the corner adatoms (the B-atoms) is greater than that on the center adatoms (the C-atoms). Moreover, there is an electron density asymmetry between the two triangular subcells of the (7×7) surface unit cell.

At $V_s = -0.8$ eV (Fig. 6b) the principal contribution to the tunneling current comes from the dangling electrons on the rest atoms and on the corner vacancies.

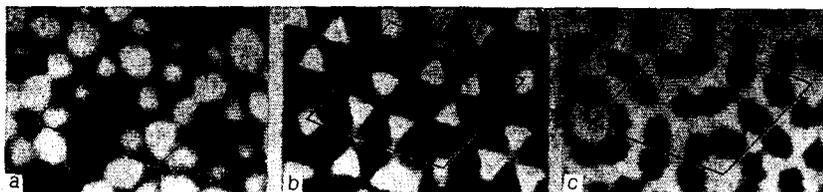


FIG. 6. STM images of the Si(111)-(7×7) surface for various sample voltages V_s . V_s (in volts): a) -0.35 ; b) -0.8 ; c) -1.7 .

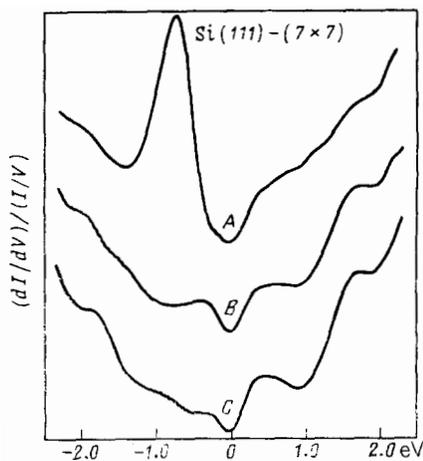


FIG. 7. Density of electron states at: curve A) the rest atoms; B) corner adatoms; C) center adatoms.

At $V_s = -1.7$ eV the image of the surface due to the distribution of the density of states corresponds to the Si-Si valence bonds (Fig. 6b).

These results are in complete agreement with the curves shown in Fig. 7 for the energy dependence of the local density of states on the adatoms and rest atoms. Curve A shows the density of states on the rest atoms. A characteristic feature of this curve is the presence of a strong maximum at -0.8 eV, which corresponds to a nearly full band of surface states localized on the rest atoms.

There is also a surface band with a maximum local density of states in the neighborhood of the adatoms (curves B and C in Fig. 7). Curve B corresponds to the corner adatoms and curve C to the center adatoms.

Curves B and C have their maxima at the energy $E_1 = -0.4$ eV below the Fermi level corresponding to an occupied band and at $E_2 = 0.5$ eV, corresponding to a partially filled band of dangling-bond surface states on the adatoms. The maximum in the density of states at the energy -0.4 eV corresponds to the situation where there is no more than one electron on each adatom site. If a single adatom has two electrons with opposite spins, the energy of each electron increases by an amount characteristic of the Coulomb repulsion, and as a result there is a second maximum at an energy 0.5 eV above the Fermi level. The maxima in the density of states at -1.7 and $+1.5$ eV correspond to surface bands with electrons which form the Si-Si valence bonds.

If the corner vacancy is electrically neutral, then the 19 electrons that form dangling bonds have the following distribution: one electron is in the corner vacancy, twelve of the eighteen remaining electrons form a completely filled band

of dangling bonds on the six rest atoms, and the last six electrons correspond to a partially filled band of dangling bonds on the twelve adatoms.

In this situation we can speak of a charge transfer from the adatoms to the rest atoms.

Since the intensity of the electron density maximum at the corner adatoms (curve B) is greater than that at the center adatoms (curve C), while that of the unfilled bands is less, we can assume that charge is transferred principally from the center adatoms. The center adatoms have two neighboring rest atoms each, and the corner adatoms have one; therefore charge transfer from the center adatoms is more probable.

The degree of filling of the dangling-bond electron states at the corner adatoms is greater than those on the center adatoms.

5. Chemical reactions on the Si(111)-(7x7) surface. As has been mentioned above, the use of scanning tunneling microscopy affords the unique possibility of studying chemical reactions on surfaces, of determining the spatial distribution of the reacted atoms and the interrelation between the electron structure of the surface and the reactivity of various surface atoms.

In Ref. 11 STM was used to study the chemical reaction on the Si(111)-(7x7) surface interacting with NH_3 .

It was determined from the experimental results that the different atoms of the reconstructed surface are not chemically equivalent. Figure 8a shows the topography of a clean Si surface at a voltage $V_s = 0.8$ V. In this case the current was determined by tunneling into unoccupied sample states having an energy between E_F and $E_F + 0.8$ eV. Under these conditions all 12 adatoms are clearly seen in the STM image (Fig. 8a).

Figure 8b shows an image of the same region of the surface, also taken with 0.8 V on the sample, after interaction with NH_3 at an exposure $\sim 1L = 10^{-6}$ torr·s. In this case the images of some of the adatoms, especially the center ones, are missing. The disappearance of the adatom images as a result of the reaction with the NH_3 in a consequence of the change that occurs in the electronic structure of the surface during the chemical reaction. If the voltage is increased to $+3$ eV, all the adatoms become visible again, but the image of the surface shows a small number of defects (Fig. 8c).

Preservation of the basic topographic structure of the Si(111)-(7x7) surface with an applied voltage of 3 V indicates that the surface atoms form chemical bonds mainly through the dangling bonds and not as a consequence of the breaking of Si-Si valence bonds.

In order to understand the nature of this chemical reaction we should compare the topographical image and the

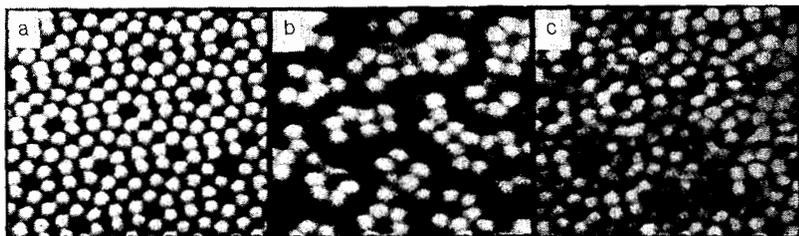


FIG. 8. STM image of the clean Si(111)-(7x7) surface for $V_s = 0.8$ V (a); and also for the same surface partially reacted with NH_3 at $V_s = 0.8$ V (b) and 3 V (c).

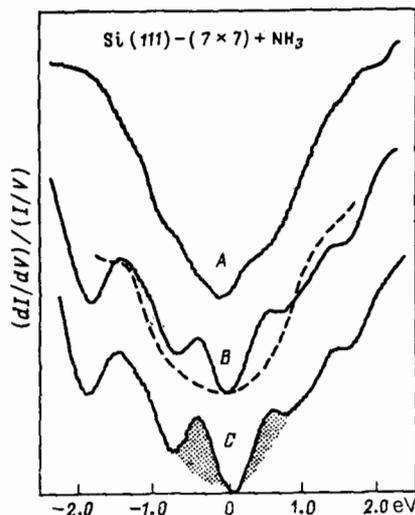


FIG. 9. Density of electron states of the Si(111)-(7×7) surface after reaction with NH₃. Curve A corresponds to the reacted rest atoms; curve B (dashed curve): reacted corner adatoms; B and C (solid curves): unreacted corner and center adatoms.

energy dependence of the local density of states at atomic resolution for the clean and the reacted Si surface.

While we are able to draw conclusions about the reaction of NH₃ with adatoms from the topographical image of the surface, in order to follow the reaction involving the rest atoms it is necessary to study, with atomic resolution, the changes in the spectrum of the density of states after the reaction. Figure 9, which is taken from Ref. 11, shows, for partially reacted Si surface, the energy dependence of the local density of states on the rest atoms (curve A), on the reacted corner adatoms (dashed curve B), and on the unreacted adatoms (solid curves B and C).

After reaction with NH₃ the spectrum of the density of states on the rest atoms no longer has the maximum at -0.8 eV which is characteristic of the clean surface and which corresponds to the completely filled band of dangling-bond surface states (Fig. 9, curve A). The density of states on the reacted adatom no longer contains the maxima at energies -0.4 and 0.5 eV, which corresponds to a partially filled band of dangling electrons on the adatoms. These peaks disappear because the dangling electrons on the reacting Si atoms form valence bonds with the NH₃ during the chemical

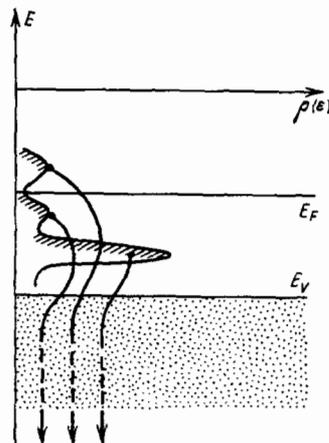


FIG. 10.

reaction. The density-of-states peaks corresponding to the surface bands are lowered by an amount equal to the binding energy; they shift downward (Fig. 10) and mix with the bulk states. The energies of these states after the reaction lie more than 2 eV below E_F , and consequently they are not seen in Fig. 9.

The disappearance of the images of the reacted adatoms on the Si surface of 0.8 eV is due to the lowering of the energy of the corresponding band of surface states and to the absence of a maximum in the density of states in the range from E_F to $E_F + 0.8$ eV. As a result of this process the tunneling current decreases and the reacted adatoms show up in the image as holes.

On the unreacted adatoms (solid curves B and C in Fig. 9) the maxima in the density of states increases. It follows from Figs. 8 and 9 that only some of the adatoms participate in the reaction with NH₃, while all rest atoms have entered into reaction.

As we have already mentioned, the chemical bond is formed through the dangling electrons on the surface atoms. The recovery of the image of the Si surface structure when the positive voltage on the sample is increased lends support to this conclusion. At the same time, the dangling bonds on the rest atoms form a completely filled band of surface states. Therefore, in order for the rest atoms to react strongly with the NH₃, there must be a back transfer of charge from the rest atom to the adatom.

When NH₃ is deposited on the Si surface, there is a change in the potential at the positions of the electrons which are located on the nitrogen atoms but do not form valence bonds with the hydrogen: a vacuum potential barrier is substituted for the periodic potential of the Si surface. The N atom has two electrons that do not form valence bonds with H. If the NH₃ molecule is on the Si surface one of these electrons can transfer into a state of the continuous spectrum of the partially filled surface band; i.e., it can transfer to an adatom by virtue of the bound-state level broadening caused by the presence of the periodic potential on the surface.

In this case there is an extra positive charge on the nitrogen. From there on there are two possible ways in which the reaction might go:

a) One of the H atoms transfers to an adatom or to a neighboring rest atom, forming a Si-H bond. One of the rest atom electrons transfers to the N, since there is an excess positive charge on the N atom. The last stage of the reaction is the formation of a Si-NH₂ valence bond by the dangling electron remaining on the rest atom and one of the nitrogen electrons.

b) After the excess positive charge appears on the N, one of the dangling electrons on a rest atom transfers to a nitrogen atom, and the excess negative charge on the rest atom vanishes. Thereafter, the most probable events are the formation of a chemical bond of a nitrogen valence electron with a dangling electron on a rest atom and the dissociation of the NH₃ into H and NH₂ with the formation of a Si-H chemical bond on an adatom or on a neighboring rest atom. Of highest probability is the formation of Si-NH₂ on the rest atoms and Si-H on the adatoms. As a result of the reaction the excess negative charge on the surface rest atoms vanishes.

The back-transfer of charge occurs mainly towards the center adatoms, since the rest atoms each have two neigh-

boring center adatoms and one neighboring corner adatom. Therefore the center adatoms have a greater reactivity than do the corner adatoms. After the back transfer of charge, dangling bonds exist both on the rest atoms and on the adatoms. The rest atoms, however, have a considerably greater reactivity than the adatoms: there are practically no remaining unreacted rest atoms. The reason for this behavior may be that the dangling electrons on the adatoms are more delocalized than the rest atoms because of the strong interaction with the atoms of the second surface layer lying directly below the adatoms. The maximum of the local density of states on the adatoms is considerably lower than that on the rest atoms, while the width is greater.

In conclusion, we have reported how the use of the scanning tunneling microscope has provided for the first time the possibility of observing the spatial distribution of atoms that have reacted on the Si surface and has made it possible to

establish that the reactivity of various surface atoms is directly related to the presence of localized dangling bonds.

- ¹G. Binnig and H. Rohrer, *Helv. Phys. Acta* **55**, 726 (1982).
- ²J. A. Stroscio, R. M. Feenstra, and A. P. Fein, *Phys. Rev. Lett.* **58**, 1668 (1987).
- ³J. A. Stroscio, F. M. Feenstra, and A. P. Fein, *Phys. Rev. B* **36**, 7718 (1987).
- ⁴J. Tersoff and D. R. Hamann, *Phys. Rev. B* **31**, 805 (1985).
- ⁵K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, *J. Vac. Sci. Technol. A* **3**, 1502 (1985).
- ⁶G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, *Phys. Rev. Lett.* **50**, 120 (1983).
- ⁷D. J. Chadi, *Phys. Rev. B* **30**, 4470 (1984).
- ⁸L. C. Snyder, *Surf. Sci.* **140**, 101 (1984).
- ⁹E. G. McRae and P. M. Petroff, *Surf. Sci.* **147**, 385 (1984).
- ¹⁰R. J. Hamers, R. M. Tromp, and J. E. Demuth, *Surf. Sci.* **181**, 346 (1987).
- ¹¹R. Wolkow and Ph. Avouris, *Phys. Rev. Lett.* **60**, 1049 (1988).

Translated by J. R. Anderson