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Effect of Relaxation and Reconstruction on the Electronic-Energy-Level Structure of the Si(111) Surface

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Intrinsic surface electronic energy states for the ideal (1×1), relaxed (1×1), and reconstructed (2×1) Si(111) surfaces have been successfully calculated by use of the self-consistent scattered-wave cluster model. For both ideal and relaxed structures, we find three bands of surface states. For (2×1) reconstruction our dangling-bond surface band splits into two overlapping bands. Our results account for all the observed features in photoemission experiments on Si(111) surfaces.

The electronic energy structure for the Si(111) surface has been the subject of many current investigations.[1-10] In a recent paper Appelbaum and Hamann[2] calculated the electronic structure of the Si(111) surface with and without relaxation. In both cases they predicted a dangling-bond surface state, S_1, lying in the energy gap. The exact location and the width of this band are still in dispute.[4,5,7-9] For the relaxed case, they also found two additional surface states (S_2 and S_3, both in the valence band) which are localized in the back bonds of the surface atoms.

Here we present the results for the electronic-energy-level structure for the ideal and relaxed Si(111) surfaces, calculated *self-consistently* by use of the scattered-wave cluster model.[11,12] It is well known[10] that after cleavage in ultrahigh vacuum at room temperature the surface reconstructs to Si(111) (2×1). Therefore, to improve the physical realism of our analysis, we have simulated the effect of this reconstruction on the electronic structure. We have also demonstrated that cluster studies can be successfully used for understanding surface electronic structure. In fact, this is the first time that surface reconstruction has been investigated by the cluster method. The power of the method lies in its simplicity and the fact that it is fully self-consistent.

The basic idea behind the cluster model is that the electronic structure can be described reasonably by local order.[13-15] Thus, without including too many atoms, an adequate approximation to the solid can be made. In covalently bonded semiconductors, bulk electronic structure can be calculated[15] by considering a cluster whose dangling orbitals have been saturated with hydrogen atoms. For Si, this procedure is well justified because the Si-H bond strength[16] (3.1 eV) is not too different from the Si-Si bond strength[16] (3.3 eV). To apply the cluster model to surface calculations, one chooses a cluster having proper point-group symmetry, with appropriate dangling bonds left unsaturated. For example, an Si_4H_{10} cluster is the smallest cluster that may be used for the bulk, and Si_4H_9 for the Si(111) surface. Even such small clusters give[14,15] eigenvalues corresponding to the short-wavelength as well as long-wavelength Bloch waves, and produce a valence band of width ~12 eV. By making the cluster bigger, one picks up eigenvalues at intermediate $\vec{k}$ points without substantially altering the total width of the valence band. Beyond a certain point, addition of more atoms to the cluster does not change any qualitative conclusions. Their effect on the density of states can be simply simulated by appropriately choosing the broadening parameter σ in the equation

$$D(E)=\sum_i \frac{N_i}{(2\pi\sigma)^{1/2}} \exp\left(-\frac{(E-\epsilon_i)^2}{2\sigma^2}\right). \qquad (1)$$

In our calculations the orbital relaxation effects were included in determining the binding energies, ϵ_i, of all occupied orbitals by employing the transition-state method.[11] Furthermore, to improve the physical realism of the scattered-wave cluster model for surface studies, overlapping atomic spheres[12] were used and the calculations were carried to full self-consistency.

To investigate the electronic structure of the Si(111) surface, one must choose a cluster having the C_{3v} point-group symmetry. The cluster $Si_{13}H_{21}$ is suitable because it represents a central silicon atom located on the Si(111) face and includes up to second-nearest-neighbor Si atoms. From band-structure calculations,[9, 17] one knows that the third- and higher-neighbor interactions only affect the detailed shape of the bands and thus can be neglected for our present purposes. The cluster $Si_{13}H_{21}$ has three layers of silicon atoms along the z axis or [111] direction. The first layer has seven silicon atoms (dangling bonds) and the two below have three silicon atoms each. Such a cluster should give a reasonable description of the bulk and surface effects. To get more quantitative results about the dangling bond we further saturated the six peripheral Si atoms with hydrogens and focused our attention on a single dangling bond in the $Si_{13}H_{27}$ cluster. The single dangling-bond state in $Si_{13}H_{27}$ appears as a band in the $Si_{13}H_{21}$ cluster.

The density of states computed from Eq. (1) ($\sigma = 0.25$ eV) for the ideal (1×1) $Si_{13}H_{27}$ cluster is shown by solid lines in Fig. 1(a). The transition-state binding-energy scale shown at the bottom of Fig. 1 has no absolute significance because of the presence of the outer sphere which surrounds the entire cluster. The energy scale at the top of Fig. 1 is obtained by approximately aligning the dangling-bond surface state with the Fermi level, E_F. The overall shape of the curve and the total width of the valence band are in good agreement with the superposition of the *bulk and surface* densities of states [shown by dash-dotted line in Fig. 1(a)] as measured by Rowe and Ibach using uv-photoemission spectroscopy.[7] The calculation successfully accounts for all the observed structure qualitatively. In Fig. 1(b) the essential surface-related structure has been shown. It was calculated with use of the $Si_{13}H_{21}$ cluster and shows *bands* of surface states.

The special features arising as a result of the surface effects are as follows. First of all, one sees a peak near the top of the valence band due to the half-filled state S_1 (dangling bond). An examination of the wave function and charge distribution for this state reveals a high degree of charge localization in primarily the p_z orbital of the top layer of silicon atoms. The band S_2 has most of its charge localized on the first two layers of silicon atoms having primarily the orbital character p_x and p_y. Further surface-related structure, S_3, appears near the bottom of the valence band. The charge is localized and has orbital s character. Thus, the three surface states discussed above are of $p_z + \epsilon s$ (S_1), p_x, p_y (S_2, doubly degenerate), and $\epsilon p_z + s$ (S_3) orbital character as discussed by others.[2] An important difference, however, is that we find these surface states for the ideal surface as well.

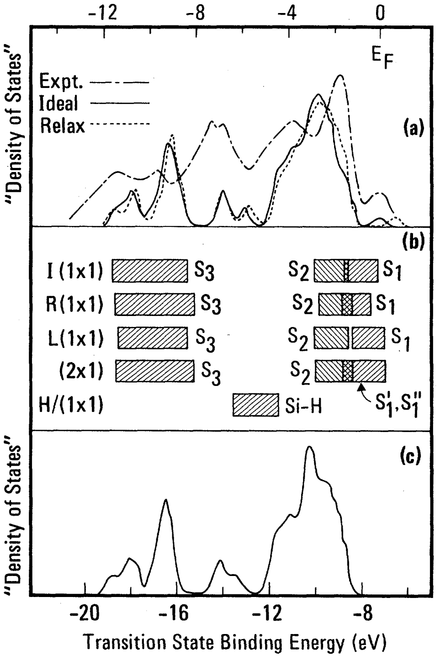

FIG. 1. (a) Computed density of states for the $Si_{13}H_{27}$ cluster. (b) Surface-state bands for $Si_{13}H_{21}$ cluster; I, ideal; R, all surface atoms raised; L, all surface atoms lowered; and (2×1) stands for reconstructed surface. $H/(1\times1)$ is hydrogen chemisorbed on Si(111) surface. (c) Computed density of states for $Si_{13}H_{28}$ cluster.

We next investigate the effect of surface relaxation.[2] The computed density of states for such a relaxed $Si_{13}H_{27}$ (1×1) cluster is shown by dotted lines in Fig. 1(a). Clearly, the overall structure is similar to the ideal case. The state S_1 has shifted higher in energy. This is consistent with intuitive arguments that the dangling bond becomes more p_z-like and back bonds become more s-like upon inward relaxation. Because of an increased s contribution in the back bonds, we observe an excess total charge on the surface layer of silicon atoms. We conclude that S_1, S_2, and S_3 are present for ideal as well as relaxed surfaces, in contrast to some earlier calculations[2] where S_2 and S_3 appear only upon relaxation.

Now let us study the effect of (2×1) reconstruction on the electronic structure of the Si(111) surface. We adopt Haneman's[10] model for the (2×1) reconstruction. For the cluster $Si_{13}H_{27}$, when the central Si atom was raised by 0.34 a.u., we found that S_1 shifted down in energy by $\sim$0.3 eV and became more s-like. When the central Si atom in the $Si_{13}H_{27}$ cluster was lowered by 0.21 a.u., S_1 moved up in energy by $\sim$0.3 eV and became more p_z-like. By combining these two results, we could deduce the approximate level structure for a (2×1) reconstruction. We concluded that upon reconstruction S_1 splits into two closely lying states S_1' and S_1'' separated by about 0.5 eV. However, S_1' and S_1'' broaden into two half-occupied overlapping bands in the $Si_{13}H_{21}$ cluster as illustrated in Fig. 1(b). Thus, our calculation, based on Haneman's model of reconstruction, suggests a two-dimensional "metallic" behavior at the surface. A small energy gap may, however, open up depending upon the reconstruction parameters. It is interesting to comment that Tosatti and Anderson[18] were unable to predict (2×1) reconstruction of Si(111) strictly as a consequence of surface *metal-insulator* phase transition.

Finally, let us examine the effect of hydrogen chemisorption on Si(111) by using the $Si_{13}H_{28}$ cluster, where all the dangling bonds are saturated. The computed density of states is shown in Fig. 1(c). One sees that the dangling-bond surface state, S_1, has disappeared and a new state due to the Si-H bond has appeared about 3 eV below the valence-band edge. Densities of states shown in Figs. 1(a) and 1(c) are not expected to be drastically different in shape because only one energy state has shifted from the gap region to about 3 eV below. Furthermore, both curves are dominated by the bulk density of states. If the chemisorption on the $Si_{13}H_{21}$ cluster is considered, all seven Si-H bonds form a band shown in Fig. 1(b). A detailed examination of the wave function reveals that the states S_2 and S_3 are delocalized. These results are in good agreement with the experimental observations.[6]

We also carried out calculations for the cluster $Si_{14}H_{18}$ which has six layers of silicon atoms along the [111] direction. The surface states S_1, S_2, and S_3 were easily recognizable in this model with and without relaxation, but the entire spectrum was rigidly shifted by about 1.5 eV as a result of the presence of a different outer sphere. We have completed calculations for the ideal Si(100) surface by using the $Si_{18}H_{22}$ cluster. No dangling-bond states were found for this surface. The highest occupied surface state has orbital character p_z, where z is normal to the (100) surface. The lowest unoccupied surface state is essentially p_y type. Detailed results will be published subsequently.

In summary, for the Si(111) surface we found three surface states, regardless of the surface relaxation. Orbital characters of these states agree with previous studies.[2] For Si(111) (2×1) our calculation makes a novel prediction that the reconstructed surface is perhaps "metallic" or a narrow-band-gap semiconductor depending *upon the reconstruction parameters.* In conclusion, it can be stated that simple clusters chosen appropriately can be successfully used for calculating the electronic structure of solid surfaces.

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Sputtering of Nb and Au by (*d*, *t*) Neutrons*

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Neutron-sputtering ratios are reported for (*d*,*t*) neutrons incident upon Nb and Au foils. The measured ratios are lower than most previous results. For annealed Au as well as for cold-worked Nb the best values for the sputtering ratios are in the range $S_n \lesssim (1.2-2.5)\times 10^{-5}$. These results are in good agreement with theoretical predictions. A careful search for neutron-induced micron-sized particles yielded negative results.

Neutron-sputtering ratios have been measured by various experimenters[1-12]; however, the results are in poor agreement and are generally higher than ratios predicted by theory.[13-15] Exceptionally high fast-neutron yields have been observed by Kaminsky and Das[8,9]; they report sputtering ratios as high as 0.25 ± 0.1 atoms per (*d*, *t*) neutron for cold-worked Nb foils. The sputtered material at these high yields was observed to be primarily in the form of micrometer-sized chunks. Guinan[16] has developed a theory to explain neutron-triggered emission of chunks on the basis of stored internal energy. However, a theoretical treatment by Weertman[17] questions the possibility that micron-sized chunk emission can be caused by fast neutrons at the fluence levels used in Kaminsky and Das's experiment.

In summary, the available experimental results and the theoretical predictions of neutron-sputtering ratios, cited above, range over four orders of magnitude. That is, from $S_n \gtrsim 10^{-5}$, according to theory, to $S_n > 10^{-1}$, according to some experiments. At the present time it appears difficult to postulate theoretical mechanisms to explain the highest measured sputtering ratios and the associated micron-size particle emission.

In this paper we report some results for Au and Nb following an extensive series of (*d*, *t*)-neutron-sputtering experiments on various metals and nonmetals. Figure 1 shows the general arrangement of our sputtering targets, collectors, and the (*d*, *t*)-neutron source. All measurements reported here were made at the Lawrence Livermore Laboratory using their rotating target neutron source (RTNS). The neutrons were produced in a thin tritiated Ti target which was bombarded with 400-keV D^+ ions. A source strength of $(3-5)\times 10^{12}$ neutrons/sec was attained in a source spot of ~ 1 cm^2.

Targets were prepared from high-purity commercially available materials such as Materials Research Corporation, Marz-grade Nb. Most collectors or catchers for sputtered material

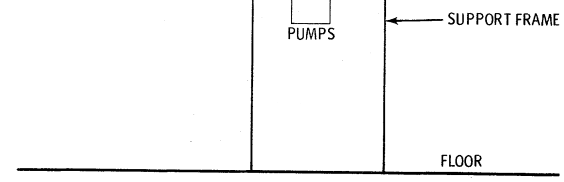

FIG. 1. Experimental arrangement at the (*d*,*t*)-neutron source.