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Hydrogen Chemisorption on Si: A New Type of Chemisorptive Bond

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Theoretical studies of the bonding of atomic H to the Si(100) surface indicates that a strong but unconventional covalent bond can be formed between the H and a Si atom in the second layer whose conventional tetrahedral bonds are already saturated.

During the last few years an extensive experimental and theoretical effort[1-10] has been mounted to understand the chemisorptive bonding of H to the elemental semiconductors Si and Ge. For the case of H on Si(111), excellent agreement has been obtained between theory and experiment with regard to electronic and vibrational properties. In this and other cases studied, H bonds to the semiconductor substrate via atoms at the surface that have broken bonds. More recently, H has been shown capable of causing stoichiometric or corrosive modification of a H-covered Si(111) surface, yielding the so-called trihydride phase of Si(111).[3] While it has been suggested that surface vacancies nucleate this phase,[3] no atomistic mechanism has been proposed for changing a H-saturated Si(111) surface with Si-H surface bonds into one missing the outer Si layer and having in its place a Si-SiH_3 surface structure.

In this Letter, we report a novel result which has arisen in the course of a series of calculations of H interacting with a Si(100) 1× 1 surface. These calculations show that atomic H is capable of forming a strong chemical bond to subsurface (second layer) Si atoms, in spite of the completely saturated chemical environment of these atoms. This chemisorptive bond is not activated, and leads to a marked weakening of the Si-Si bonds between surface and subsurface Si atoms. Although the detailed results pertain to one particular surface geometry, a simple interpretation of the state forming the bond suggests parallel results for any relaxed or reconstructed Si surface with approximately tetrahedrally coordinated subsurface Si open to the vacuum. We will discuss experimental evidence that a similar bond exists on Si(110). We believe such bonds could be the precursor states responsible for the corrosive modification of hydrogenated Si surfaces.

The calculations are fully self-consistent, employing the local density approximation for exchange and correlation, and a model potential for the Si^{4+} core, and parallel those previously reported for clean[11] and hydrogenated Si surfaces.[9] The local geometry of the Si(100) 1× 1 surface is shown in Fig. 1. A monolayer of H atoms is po-

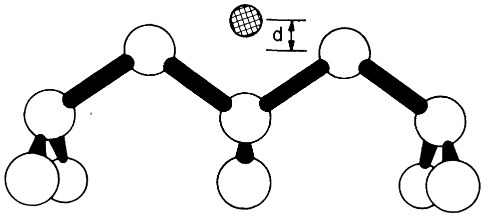

FIG. 1. A schematic sketch of a portion of the Si(100) 1× 1 surface, showing the position of the H monolayer, hatched circle (a distance *d* from the surface plane) over the second-layer Si atoms. The broken bonds in this model extend above and below the plane of the figure.

sitioned to lie over the second-layer Si atoms, at a distance d from the surface. Because the H atoms are separated by 7.26 a.u., we believe the chemical properties of the H monolayer and a single H atom interacting with this surface are similar. The interaction between the Si surface and the H was calculated from the force on the H via the Hellmann-Feynman theorem[12] and the self-consistently determined charge density at ten H-Si separations ranging from $d=0.2$ to 3.8 a.u., assuming a frozen Si substrate. For $d \geq 2.2$, the surface matching plane was placed between the second and third Si layers, for $d \leq 2.2$ between the third and fourth Si layer. Duplicate calculations at $d=2.2$ exhibited excellent convergence with respect to matching-plane placement.

To discuss the H-Si system, we review the electronic structure of the clean Si(100) 1×1 substrate. The surface has two bands of gap surface states: one dangling-bond–like, oriented along the surface normal; the other bridgelike, confined near the intersection of the surface plane and the plane of the broken surface bonds. They accommodate the two electrons supplied by the broken bonds, with the dangling-bond band almost completely filled. The presence of the H, positioned midway between the surface atoms and at right angles to the plane of the broken bonds, has little effect on these states. This is in contrast to our previously reported study of H on Si(100), in which the H, directly over the Si surface atoms, forms a covalent bond via H 1s, Si dangling-bond hybridization. It is also in contrast to the case where the H is positioned midway between surface Si atoms but in the plane of the broken bonds. In that case, calculations show hybridization occurring between the bridge band and the H s state.

Because of the insensitivity of the broken-bond-derived surface states to the H overlayer, the initial interaction of the H with the Si is weak. The total charge density for the case $d=3.7$ a.u., plotted on a plane normal to the surface and passing through first- and second-layer Si atoms, in Fig. 2(a) shows only small distortions compared with the clean surface (see Fig. 16, Ref. 11). These are sufficient, however, to produce an attractive force on the H plane, plotted in Fig. 3. With decreasing d, we find a gradual decrease in the inward force on the H, accompanied by the polarization of the charge density around and just above the second-layer Si atoms, as is seen in Fig. 2(b). This charge buildup, caused by the H, has its spectral origin in a surface state which has been split downward by 0.5 eV (for $d=2.2$) from a bulk band near -3.5 eV (referenced to the valence-band maximum). The results obtained for $d \geq 2.2$ extrapolate to zero force at $d \approx 1.8$, which would represent a weak polarization-type bond between the substrate and the H overlayer with a binding energy per H of ~ 1.5 eV[8] [inferred from integrating the force law (Fig. 3) and making a rough extrapolation for large distances]. This is, indeed, the sort of behavior observed in a recent calculation of H binding on the Al(100) surface for H over the second-layer atom.[13]

By contrast, the actual force on the H for $d < 2.2$ reaches a plateau and then increases dramatically with decreasing Si-H separation. The

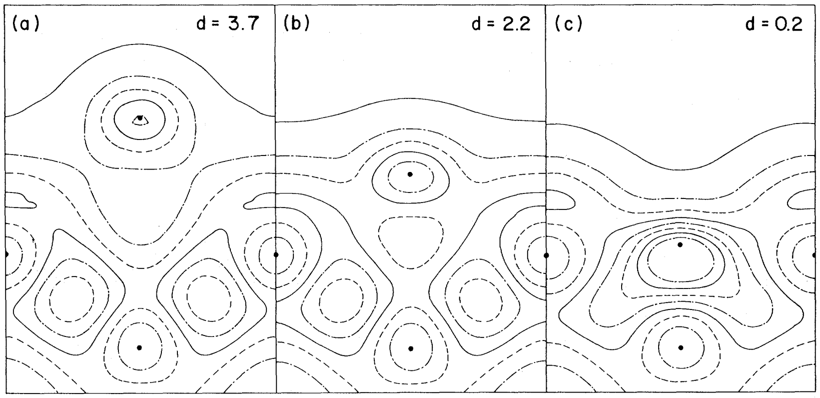

FIG. 2. Contours of constant charge density are plotted for three H–surface-Si separations on a plane normal to the surface and passing through the H atoms (small closed circles) and first- and second-layer Si atoms (larger closed circles). The contours, spaced 1.5×10^{-2} a.u. apart, begin at 5×10^{-3} a.u. with the solid lines in the vacuum region (upper portion of the figure) and alternate line type from solid to dot-dashed to dashed to solid for clarity. Like contour types are separated by 4.5×10^{-2} a.u. For reference, the average Si valence charge density is 2.95×10^{-2} a.u.

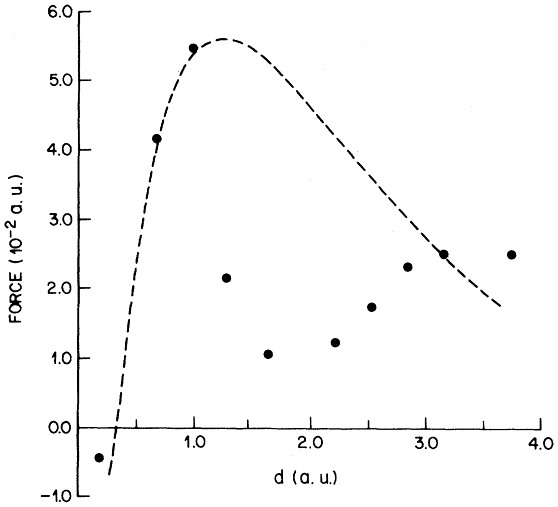

FIG. 3. The calculated force on the H overlayer is plotted (solid circles) as a function of Si-H separation *d*. The dashed curve is the Morse-potential fit previously obtained for H interacting with surface Si atoms, but with its origin referenced to the second layer.

force peaks near $d \approx 1.0$ and decreases rapidly to zero near $d = 0.25$. This true equilibrium[14] places the H 2.76 a.u. above the second-layer Si atoms, close to the covalent-bond length of a Si-H bond. The additional binding of approximately 1.2 eV, calculated from the force law between $d = 2.2$ and 0.25, suggests a covalent bond has formed. The fact that similar second-layer bonding was not seen in the Al-H study may represent a significant difference in the behavior of metals and semiconductors, or may be a consequence of the fact that the Al lattice potential was included only by first-order perturbation theory.[13]

To compare this bond with a conventional one, we have plotted the Morse-potential fit to the calculated force law for the case of H above surface Si atoms, previously obtained,[9] as a dashed line in Fig. 2. No adjustments were made except for the obvious change of origin to the second layer. Near equilibrium they are similar, but the force in the present study is strongly reduced between $d = 1.0$ and $d = 3.0$, which we interpret as the effect of the surface layer screening out the H, second-layer–Si interactions. The force minimum at $d = 1.8$–2.0 is near where one would place the effective surface dielectric plane[15,16] (inferred from jellium calculations to be in an electron density region of approximately $\frac{1}{3}$ of the bulk density).

The bonding energy of H to second-layer Si atoms is estimated to be approximately 1 eV less than to surface Si atoms by integrating the area between the dashed curve and the points in Fig. 3. This reduction might seem to be inconsistent with the nearly equal bond length and force constant found in both cases. However, the presence of the H reduces the first-layer Si bond charge density by 20% relative to the second [Fig. 2(c)], and if we assume a 20% reduction of two 2.3-eV Si-Si bond energies,[17] the loss of 1 eV of total bond energy can be accounted for. The weakened Si-Si bonds presumably expand, although determining the extent of the expansion is beyond the present study.

What is the nature of this bond? An examination of the total charge density for $d = 0.2$ strongly suggests a multicentered bond analogous to those found in the boron compounds, particularly the boron hydrides.[18] In a simple tight-binding interpretation, the bond here is made up from valence-bond orbitals, centered on the bond charge between the first- and second-layer Si atoms,[19] and the H 1*s* state. The bonding combination, which should be low in energy,[8] manifests itself as a deep surface state at − 10.5 eV. The antibonding combination shows up as a partially occupied gap surface state and the nonbonding combination contributes to the weakened Si-Si back bonds.

In addition to the three states discussed above, which are distinctly identifiable only for small *d*, the "polarization" surface state previously noted for large *d* continues to exist and drops in energy to − 5.3 eV at equilibrium. This is ~ 1.5 eV lower than the prominent surface state predicted theoretically and confirmed experimentally for conventionally bonded H on Si(111).[4,6] Ultraviolet photoemission studies of atomic H adsorption on Si(110) shows the "conventional" spectral features for high substrate temperatures (350°C), but show additional states in the region 1–2 eV below the principal peak at room temperature.[20] This was tentatively interpreted as a result of additional H weakly bound at nontetrahedral subsurface sites, and the present results both support this interpretation and provide a model for the bonding involved. We suggest that such bonds may also play a role in H-incorporated amorphous Si and Ge, since the conditions under which they are formed should provide a high concentration of atomic H.[21]

One of us (K.H.T.) was a summer Research Associated at Bell Laboratories, Murray Hill, N. J.

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Resolved Quadrupolar Transition in TiO_2

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We report an investigation of the direct forbidden absorption edge of TiO_2. For the first time we have resolved the weak quadrupolar 1*s* exciton and measured its binding energy. Taking into account polaron effects, we estimated the bare electron effective mass in the Γ_1 minimum of the conduction band and obtained a fairly reasonable value of $3m_0$.

The forbidden exciton series in semiconductors have long been a subject of interest. However, all experimental work was restricted to SnO_2 and Cu_2O. SnO_2 belongs to the $D_{4h}{}^{14}$ symmetry group. At low temperature, the absorption edge spectrum exhibits a sharp hydrogenlike series of exciton lines when the light is polarized perpendicularly with respect to the fourfold C axis ($E\perp C$). The quadrupolar character of the transition associated with the $n=1$ exciton state has been well established.[1] Cu_2O has a cubic symmetry (point group O_h) but a compression along any of the three equivalent fourfold axes (001) reduces its symmetry into a tetragonal one. The point group is again D_{4h}, with the C axis parallel to T. Experimental results[2] show that, under (001) uniaxial stress T, the forbidden yellow series disappears in the $E \parallel T$ configuration and is only observed in the $E\perp T$ configuration. In other words, the forbidden exciton series of Cu_2O reduces to the forbidden one of SnO_2, with the same selection rules, under tetragonal compression.

In this Letter we identify TiO_2 which belongs to the same $D_{4h}{}^{14}$ symmetry group as SnO_2, as being a new material with a direct forbidden absorption edge. This contrasts with recent reports which identifies TiO_2 as an indirect-band-gap semiconductor.[3-5] We resolve the weak quadrupolar 1*s* exciton state and determine the exciton binding energy. Taking into account the high values of the dielectric constant, and correcting for the associated polaron effects, we get the first estimate of the bare effective mass in the Γ_1 minimum of the conduction band.