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Self-Consistent Quantum Theory of Chemisorption: H on Si(111)

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A theoretical study of a monolayer of H chemisorbed on the (111) surface of Si is described. The length and force constant of the chemisorptive bond are determined and are consistent with molecular data. The calculated electronic spectrum of the surface is consistent with recent photoemission results.

The feasibility of a complete quantum chemistry for adsorbed layers on solid surfaces, including bond-length and force-constant determination, is demonstrated by results on the hydrogen-silicon system reported here. An H monolayer with primitive two-dimensional order has been shown to form readily when atomic hydrogen is incident on freshly cleaved Si(111) surfaces.[1] The presumed chemical simplicity of this system and our previous success with clean Si surfaces[2] suggested it as an excellent candidate for an initial study. Each surface Si atom has a single broken bond which can be saturated by an H atom. Si-H bond lengths are experimentally known to be close to the sum of the covalent radii for a wide variety of molecules,[3] so the desired geometry is empirically well determined. The saturation of all bonds reflects itself in the absence of partially occupied bands of surface states, which is a useful simplification.

The vast majority of previous studies of the electronic structure of the chemisorptive bond have used empirical models, generally with a single adatom orbital coupled to some representation of the solid Bloch states.[4] A few "first-principles" calculations have recently been reported treating chemisorption on very small clusters (self-consistent),[5] on slabs (non-selfconsisten),[6] and within a semi-infinite jellium model (self-consistent).[7]

The calculations reported here improve upon all of these previous studies by incorporating the following characteristics: (1) They are "first-principles" calculations. While model potentials representing the ions are used to smooth valence wave-function nodes, these are fixed once and for all to give accurate fits to bulk bands or atomic data. (2) A basis comparable to state-of-the-art band calculations is used to obtain well-convergent numerical solutions to the Schrödinger equation. (3) A semi-infinite geometry is employed. (4) A fully self-consistent potential is achieved which involves no steps, muffin tins, or other types of discontinuities. The exact Hartree potential is calculated from Poisson's equation, and the Wigner interpolation formula is used to approximate the exchange and correlation potential.[2]

To aid the convergence of our calculation, we smeared the proton around the nominal center of the H atom with a Gaussian weighting factor $e^{-1.5r^2}$, where r is in atomic units. The resulting potential is not sufficiently attractive near the origin, so an additional "core" potential $(-2.023+1.53r^2)\times e^{-1.5r^2}$ a.u. was added to yield the correct 1s binding energy and wave function (outside the smeared region) for the isolated H atom. This procedure gives a much more accurate representation of the physics of the problem than simply truncating the slowly converging Fourier expansion of the singular Coulomb potential.

An important step in our method involves the choice of a "matching plane," inside of which the potential is assumed to have fully healed to its

bulk values. This hypothesis is exact only in the limit of a deeply buried matching plane. For practical placement, the valence charge in the surface region never exactly cancels the ion charge in this region because of the fundamental exponential decay of the surface disturbance in a semiconductor[8] and limitations in numerical accuracy. Experience has indicated that the best way to treat the residual charge disturbance is to ignore it, and renormalize individual bands plus nearby surface states to obey, within our surface region, the integer sum rule that must in fact only be obeyed asymptotically.[8,9] To test this procedure, we performed our calculations with the matching plane between the second and third Si layer, and repeated them placing it between the forth and fifth Si layer. The resulting shift in the work function, which is extremely sensitive to overall charge shifts, was +0.13 eV, strongly validating our procedure.

Constructing the surface-charge density involves integrations over energy and the two-dimensional surface Brillouin zone (SBZ). We usually approximate the latter by sampling the points Γ and J using weighting factors which cancel two shells in a two-dimensional analog of Baldereschi's expansion.[10] Adding the points $(\Gamma+J)/2$ and $(\Gamma+3K)/4$ to our sample, which cancels seven shells, produced a 0.15-eV rms change in the surface-region potential and a +0.17-eV work-function shift, attesting to the rapid convergence of this scheme.[11]

The self-consistent surface-region potential for the expected Si-H bond length is shown in Fig. 1 as a contour plot on a plane normal to the surface and including the Si-H bond and the Si-Si bonds between the first, second, and third layers. The potential is repulsive near the Si atoms because of the effective core orthogonalization potential. It is attractive at the H site, however, and the Si-H bond potential is considerably stronger than the Si-Si bond potential. The ionization potential (IP) is 5.1 ± 0.1 eV, 0.3 ± 0.1 eV smaller than our result for clean Si. The experimental shift is 0.2 eV in the same direction.[1] The direction of this shift violates expectations based on electronegativity differences. An adsorbate which is more electronegative than the substrate typically raises the IP (i.e., O on Si), while one which is less electronegative lowers it (i.e., Cs on Si). H is somewhat more electronegative than Si, and application of Pauling's formula for fractional ionicity would lead to a dipole which increased the IP by 0.2 eV.[12] This simple argument neglects the dipole due to the dangling bond on the clean surface. The removal of that dipole could more than cancel the Si-H bond polarization, and explain the apparent discrepancy.

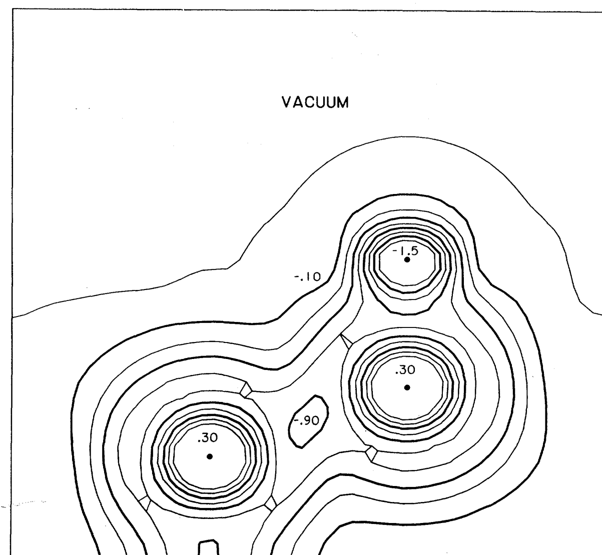

FIG. 1. Contour plot of the self-consistent potential of H chemisorbed on Si(111). The plane of the plot is normal to the surface, and the dots indicate the positions of the H, first-layer Si, and second-layer Si atoms. The contours are at 0.2 Hartree intervals, and the scale is such that the valence-band maximum falls at +0.066.

The force on the H atom was calculated using the Hellman-Feynman theorem, and found to be small and inward. Moving the H plane 0.2 a.u. inward, we repeated the calculation and found a larger outward force. The interpolated zero gave a bond length[3] of 2.73 ± 0.02 a.u., in excellent agreement with the empirical value of 2.8 a.u. used in the initial calculation. (The matching plane and SBZ sampling tests yield the ± 0.02.)

From these same results, we extracted and Si-H bond force constant of 0.175 a.u., which is identical, within our accuracy, to the measured value of 0.173 for silane.[3] The corresponding surface phonon should be observable by high-resolution electron-energy-loss spectroscopy, but has not to our knowledge been measured.

The IP shift produced by the 0.2 a.u. movement was +0.06 eV, which is in the noise. While this corresponds to a negligible dynamic effective charge as conventionally defined,[13] the surface-potential profile moves in and out nearly rigidly with the proton, and thus provides a coupling mechanism for inelastic scattering.

The notable features of the electronic structure of the Si-H surface are the disappearance of surface states in the valence-band–conduction-band gap, and the appearance of a surface-state band in the gap between the second and third valence bands (– 6.90 to – 3.62 eV at the J point in the SBZ). The charge density of this state at J (– 3.82 eV) is shown in Fig. 2. The state is clearly connected with the Si-H bond. The H "orbital" is very strongly coupled to the Si bands, however. At the J point, the surface state contributes only 48% of the charge density on H, and the band states contribute 52%. The gap containing this surface state disappears in the center half of the zone, and the surface state gets "squeezed out" to become a resonance. On the way to self-consistency, we have observed the surface state to "pop out" weakly into the gap between the first and second bands at the zone center (– 10.36 to – 7.34 eV) for an overly attractive potential, but for the converged potential it is a resonance near the bottom of the second band.

It has recently been shown that many features of the spectrum of our clean Si(111) calculations[2] can be reproduced using an empirical tight-binding model.[14] We sought to use such a model to interpolate the present results throughout the SBZ by fitting four cumulants of the H local density of states at two SBZ points. A reasonable fit required the artificial device of including a matrix element between neighboring H orbitals; with H coupled only to the nearer first- and second-layer Si orbitals, the center of gravity dispersed downwards from the zone center to the zone edge, which is opposite to our results. We believe this illustrates a difficulty inherent in relying on empirical models in new situations.

The bulk Si density of states and the local density of states at the H atom center were instead calculated using the four-point SBZ sample, and are shown in Fig. 3. This sampling is adequate to reproduce all the general features of the bulk bands, as may be seen by a comparison with Kane's detailed results.[15] The H density is distributed over the bands, but has peaks 4 and 7 eV below the valence-band edge. This structure is in excellent agreement with the enhancement of the yield seen in this region in ultraviolet photoemission from H adsorbed on annealed Si.[16] H adsorption on cleaved Si appears to give less separated peaks,[17] not clearly distinguishable within the resolution of the published data.[1]

In summary, we have reported results of a detailed and realistic theoretical treatment of a chemisorbed monolayer. These results give good agreement with the empirical chemistry of the bond and experimental data on the ionization-potential shift and spectral features. The methods we have developed should thus be able to give reliable information about a wide variety of chem-

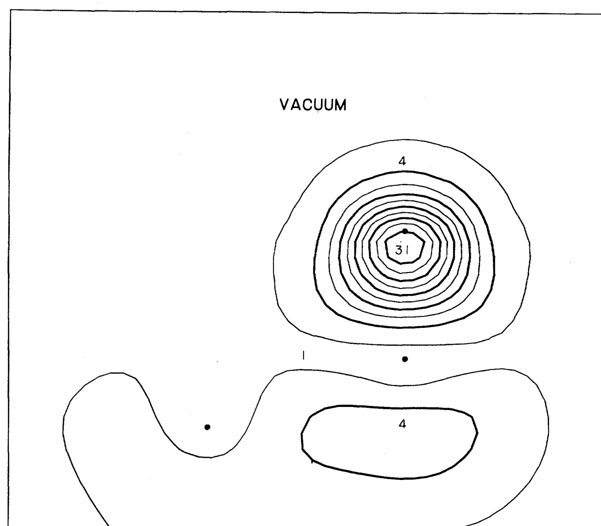

FIG. 2. Contour plot of the surface-state charge density in 10^3 a.u. The plotting plane is the same as in Fig. 1.

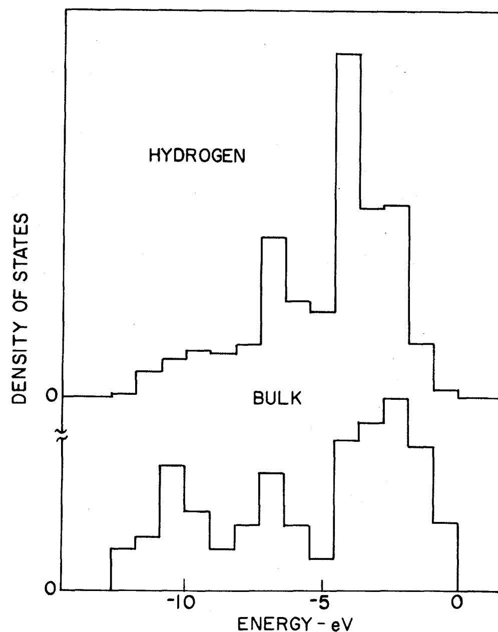

FIG. 3. Valence-band density of states for bulk Si and local density of states on the chemisorbed H atoms. The histograms are normalized for equal areas.

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Blue Anti-Stokes Electroluminescence in GaN

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Blue electroluminescence has been observed in GaN when the energy supplied to each electron is more than $48kT$ below the energy of the emitted photons. The emission increases with the cube of the current. An external power efficiency of 3×10^{-4} was obtained. Several excitation mechanisms by two hot electrons are considered.

Blue electroluminescence has been observed in GaN with an applied potential drop lower than the energy of the emitted photons. This observation contrasts with previous results obtained with GaN diodes in which the applied potential was at least four times larger than the emitted energy.[1] In the earlier experiments with metal–insulator–n-type structures, blue emission was obtained only when the metal was biased negatively with respect to the GaN; in the present work, the low-voltage blue luminescence occurs only when the metal is biased positively. Anti-Stokes electroluminescence has been seen in other materials such as GaAs[2,3] and ZnS.[4] In the work of Dousmanis *et al.*[2] the extra energy was believed to come from phonons (a refrigeration process). In the study of Nathan *et al.*,[3] higher energy initial states were populated by Auger recombination in a nearby region. Bitter, Indradev, and Williams[4] proposed that a hot electron from one region of ZnS produced a low-efficiency ($<10^{-8}$) tunneling-assisted impact excitation in a second region of the crystal. Here I have evidence for a new and different type of mechanism. This new effect was observed in several crystals grown in two different reactors on different days.

The present structure was made by the chemical vapor deposition of GaN on sapphire.[5] First an undoped n-type conducting layer was grown; then a Zn-doped layer was grown, while the partial pressure of Zn was adjusted to barely compensate the native donors (nitrogen vacancies). For reasons not completely understood, in a constant ambient Zn concentration, the concentration of Zn incorporated in the crystal appears to increase gradually during growth.[6] Therefore full compensation occurs near the middle of the Zn-doped layer, where the resistivity of the material increases suddenly by several orders of magnitude. A large-area Ohmic connection is soldered to the edge of the n-type layer while a point contact rests on the semi-insulating layer.