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Structure of Si(100)H: Dependence on the H chemical potential

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The formation energies and atomic structures of the 2×1, 1×1, and 3×1 H-terminated Si(100) surfaces were determined through first-principles total-energy calculations. The ranges of the H chemical potential (μ_H) over which these phases are stable and the equilibrium transition levels were determined. The 3×1 (monohydride plus dihydride) phase is found to be stable with respect to separation into the 2×1 monohydride and 1×1 dihydride phases. A 1×1 canted-row dihydride structure is found to be lower in energy than the 1×1 symmetric dihydride structure.

The nature of the structures formed by the interaction of hydrogen with Si(100) surfaces has been under investigation for many years. At least three different H-induced reconstructions are known to occur, and the experimental conditions required for their observation are known. The most commonly observed and best characterized surface is a 2×1 monohydride phase[1,2] in which H atoms saturate the dangling bonds of the Si dimers on the clean surface [Fig. 1(a)]. This surface can be prepared by exposing the bare surface to atomic H with the surface temperature at 650 K. Sakurai and Hagstrum[1] also observed a 1×1 phase following a room-temperature exposure and proposed that it corresponded to a symmetric dihydride termination of the surface [Fig. 1(b)]. More recently, Chabal and Raghavachari[3] discovered a 3×1 phase which they obtained by exposing the surface to hydrogen with the substrate temperature held at 370 K. From an analysis of the SiH and SiH_2 related vibrational modes they concluded that the 3×1 structure is an ordered mixture of monohydride and dihydride subunits [Fig. 1(c)]. This model for the structure of the 3×1 is supported by a recent scanning tunneling microscope (STM) study by Boland.[4] While well-ordered 2×1 and 3×1 phases were observed in the STM study, the high coverage 1×1 phase obtained by saturation exposures at room temperature was observed to be highly disordered. Apparently, the high H exposure required to produce the 1×1 phase also causes etching of the surface.

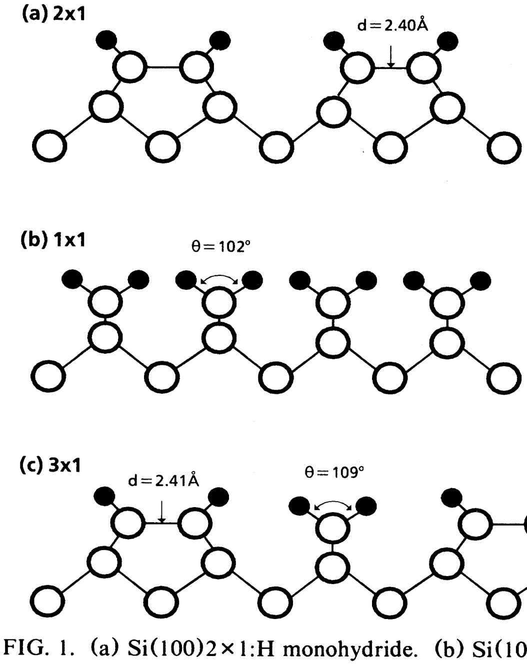


FIG. 1. (a) Si(100)2×1:H monohydride. (b) Si(100)1×1:H dihydride. (c) Si(100)3×1:H monohydride plus dihydride. Solid circles denote H atoms.

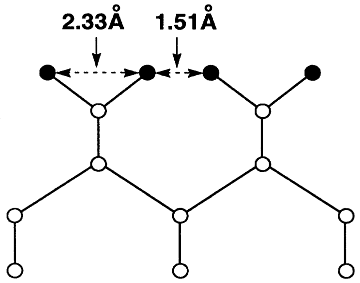
In this paper I report calculations of the surface formation energies for 2×1, 3×1, and 1×1 H-terminated surfaces as a function of the H chemical potential (μ_H). These calculations allow a comparison of the stability of structures having different numbers of H atoms. As μ_H is increased, the surface formation energy is minimized successively by the bare Si(100) surface, the 2×1 monohydride surface, the 3×1 monohydride plus dihydride surface, and then by a 1×1 dihydride structure. There exists a range of μ_H for which the 3×1 surface is lower in energy than both the 2×1 and 1×1 structures. This result implies that the 3×1 phase is stable with respect to separation into the 2×1 and 1×1 structures, and shows that the 3×1 is a thermodynamically allowed phase. The stability of the 3×1 in this regime is a consequence of repulsive interactions occurring between neighboring dihydrides in the high coverage 1×1 structure. A 1×1 canted-row dihydride structure is found to be energetically favorable with respect to the symmetric 1×1 dihydride. The canted-row structure is lower in energy because it allows the H atoms to be farther apart than in the symmetric structure (see Fig. 2).

Structural models for the 1×1, 2×1, and 3×1 phases are indicated in Fig. 1. The H coverage in these structures increases from $\Theta=1$ in the 2×1, to $\Theta=\frac{4}{3}$ in the 3×1, and finally up to $\Theta=2$ in the 1×1 phase. To determine the relative stability of these structures we must calculate their formation energies, which depend on the H chemical potential. At zero temperature the formation energy Ω may be written

$$\Omega = E + E_{\mathrm{ZPE}} - n_{\mathrm{Si}}\mu_{\mathrm{Si(bulk)}} - n_{\mathrm{H}}\mu_{\mathrm{H}} \, .$$

Here, E is the total energy, E_{ZPE} is the zero-point energy, and n_{Si} and n_{H} are the numbers of Si and H atoms. The

(a) Symmetric Dihydride



(b) Canted Dihydride

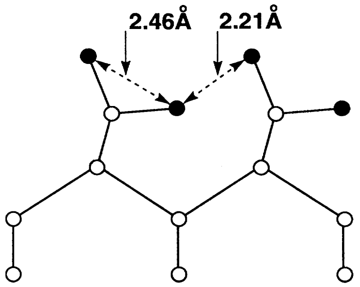


FIG. 2. (a) Si(100)1×1 symmetric dihydride. (b) Si(100)1×1 canted-row dihydride. Solid circles denote H atoms. The canted-row structure is 0.18 eV/1×1 lower in energy than the symmetric dihydride surface.

chemical potential of Si is equal to its value in bulk Si, $\mu_{\mathrm{Si(bulk)}}$. Because of the very small mass of the H atoms, the zero-point energy arising from Si-H vibrational modes can be large—of order 0.2 eV per H atom. However, for the surface structures considered here, in which the H is always bonded to a single Si atom, it is reasonable to assume that the zero-point energy is proportional to the number of H atoms, but is otherwise independent of the structure. In fact, electron-energy-loss spectroscopy data[5] indicate that the sum of the Si-H related vibrational frequencies for Si(100)2×1:H and Si(100)1×1:2H differ by only 3%. The neglect of the structural dependence of the zero-point energy therefore leads to a negligible error (less than 0.01 eV/1×1) in the relative energies of the surfaces considered here. Thus we will make what is expected to be a very good approximation:

$$E_{\mathrm{ZPE}}=n_{\mathrm{H}}e_0 .$$

For the purpose of comparing the energies of the various H-terminated Si(100) surfaces the value of e_0 is not important. However, to allow comparisons involving other H containing structures such as H_2 and SiH_4 molecules,[6] we take $e_0=0.21$ eV. This value corresponds to the zero-point energy per H atom in SiH_4. At nonzero temperatures an entropy term enters the calculation of the formation energy. This term is not expected to significantly affect the difference in the formation energies of the two-dimensional Si(100)H phases.

The total energy was calculated within the local-density functional approach.[7] A first-principles pseudopotential[8] was employed for the Si ions. The actual Coulomb potential was employed for the hydrogen ions (protons). The hydrogenated surfaces were modeled by supercells containing 10 layers of Si and one layer of H on each surface. The total-energy calculations[9,10] were performed with a plane-wave basis with an energy cutoff of 12 Ry, and eight **k** points in the irreducible zone of a 3×1 unit cell were employed in the Brillouin-zone summations.

Before beginning the discussion of the surface energetics, we briefly discuss the important features of the atomic structures. The atomic structures were obtained by force calculations. For the 1×1 phase a canted-row dihydride structure is found to be lower in energy than the symmetric dihydride. Ciraci and Batra previously examined the possibility of a symmetry lowering relaxation of the symmetric dihydride structure and found that the total energy was lowered by a small rotation of the H_2 groups.[11] The canted-row dihydride structure can be obtained from the symmetric structure by a rotation of the SiH_2 groups around an axis which passes through the *second* layer Si atoms (see Fig. 2). Thus the first layer Si atoms move through a considerable distance (0.6 Å) but retain, within 10°, their tetrahedral coordination. Such a rotation of the surface SiH_2 groups increases the distance between H atoms in neighboring dihydrides from 1.51 to 2.21 Å and thereby decreases the repulsive interactions. This occurs at the expense of an increase in strain in the Si backbonds, and a significant relaxation of the top few layers of Si occurs. The Si-Si-Si bond angles deviate from their tetrahedral values by up to 10°, but the Si-Si bond lengths remain close to the bulk value (2.34 Å). The canted-row dihydride structure is 0.18 eV/(1×1) lower in energy than the symmetric dihydride.[12] The recent STM experiments[4] did not conclusively determine the local atomic structure of the dihydride phase.

The existence of the repulsive interactions between neighboring dihydrides is also illustrated by a comparison of the H-Si-H bond angles in the symmetric dihydride and the 3×1 structure. In the 1×1 structure this angle is 102°, while it is 109° in the 3×1 structure (see Fig. 1). A closing of the bond angle in the 1×1 structure is indicative of a repulsive interaction. The calculated Si-H bond lengths are 1.50 Å in the 1×1 symmetric dihydride and approximately 1.54 Å for the Si-H bonds in the other structures. In the 2×1 monohydride structure the Si-Si dimer bond length is found to be 2.40 Å, and a similar bond length (2.41 Å) is predicted for the 3×1 structure. Calculations employing semiempirical[13,14] as well as first-principles[3,15] techniques have given similar values for the dimer bond length in the 2×1 structure: 2.37 Å (Ref. 13), 2.39 Å (Ref. 14), 2.51 Å (Ref. 3), and 2.48 Å (Ref. 15).

The calculated formation energies are shown in Fig. 3 as a function of hydrogen chemical potential. In this figure the chemical potential is measured relative to $[E(\mathrm{SiH_4})+4e_0-\mu_{\mathrm{Si(bulk)}}]/4$. Thus $\mu_{\mathrm{H}}=0.0$ is the chemical potential at which SiH_4 molecules can be formed from a reservoir of H and bulk Si with no cost in energy. For $\mu_{\mathrm{H}}<-1.28$ eV, the bare Si(100) surface has a lower energy than any of the H-terminated surfaces. In the range $-1.28<\mu_{\mathrm{H}}<-0.24$ eV the Si(100)2×1 monohydride

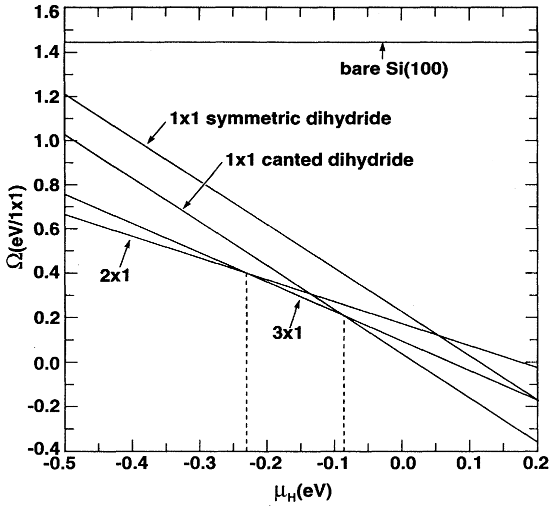


FIG. 3. Surface formation energy $\Omega(\mu_H)$ for the 2×1 monohydride surface, the 3×1 monohydride plus dihydride surface and the 1×1 canted-row and symmetric dihydride surfaces. The vertical dashed lines indicate the transition levels. The horizontal line at 1.45 eV is the surface energy of the bare Si(100)2×1 surface. The origin of the hydrogen chemical-potential scale is taken to be the chemical potential at which the formation energy of SiH_4 is equal to zero.

phase is found to be the most stable structure. A transition from the 2×1 to the 3×1 occurs when μ_H exceeds -0.24 eV. The 3×1 is stable in the range $-0.24<\mu_H<-0.09$ eV. Finally, when μ_H exceeds -0.09 eV, the 1×1 phase is stable with respect to the 3×1. It is convenient to define transition levels $\mu(A|B)$ corresponding to the values of μ_H for which the formation energies of phases A and B are equal. In particular $\mu(2\times1|3\times1)=-0.24$ eV, and $\mu(3\times1|1\times1)=-0.09$ eV.

Insight into the surface energetics may be obtained through consideration of a simple model based on the assumption that the formation energy can be approximated as a sum of the formation energies of isolated structural subunits and the energy of interaction between subunits. In this model the energy of the 1×1 canted-row dihydride phase is expressed as

$$\Omega_{1\times1}=\Omega'_{1\times1}+U\,,$$

where U is the energy arising from interactions between adjacent rows of dihydride units, including the relaxation energy due to the SiH_2 rotation, and $\Omega'_{1\times1}$ is the formation energy of an *isolated* dihydride unit. The formation energy for the 3×1 phase may be written as

$$3\Omega_{3\times1}=\Omega'_{1\times1}+2\Omega_{2\times1}\,.$$

We assume that the only important interaction occurs between neighboring dihydride units. These two relations define $\Omega'_{1\times1}$ and U. A simple relation exists between the transition levels and U:

$$U=2/3[\mu(3\times1|1\times1)-\mu(2\times1|3\times1)]\,.$$

The total-energy calculations indicate that $U=0.10$ eV. The fact that the interaction between adjacent rows of dihydrides is repulsive has important implications for the structure of the Si(100)H surface. The existence of the 3×1 phase is a consequence of a repulsive interaction. If U were negative, one would expect a transition directly from the 2×1 to the 1×1 without the existence of a stable intermediate phase.

The formation energy of any structure consisting of a mixture of monohydride and dihydride units may be estimated within this model. The energy of an $n\times1$ structure containing 1 monohydride unit and $n-2$ canted-row dihydride units in each cell may be written

$$n\Omega_{n\times1}=(n-2)\Omega'_{1\times1}+(n-3)U+2\Omega_{2\times1}\,.$$

It may be shown that $\Omega_{n\times1}>\Omega_{3\times1}$ for all $\mu_H<\mu(3\times1|1\times1)$ and that $\Omega_{n\times1}>\Omega_{1\times1}$ for all $\mu_H>\mu(3\times1|1\times1)$. In other words the $n\times1$ structure, with $n\geq4$, is always higher in energy than either the 3×1 or the 1×1. Similarly, an $n\times1$ structure comprised of one dihydride unit and $(n-1)/2$ monohydride units loses to the 2×1 phase for $\mu_H<\mu(2\times1|3\times1)$ and to the 3×1 phase for $\mu_H>\mu(2\times1|3\times1)$.

If the H-terminated surfaces were in equilibrium with a reservoir of H having a *continuous* range of chemical potential which could be tuned by changing the temperature or the pressure of the reservoir, then one would expect to observe changes in the surface H coverage when μ_H passed through a transition level. In practice the surface is not usually in equilibrium with such a reservoir. It is therefore appropriate to consider the situation where the total number of H atoms on the surface is constrained to a particular value and to determine what phase, or mixture of phases, minimizes the total energy subject to this constraint. We will assume the existence of a kinetic regime where equilibration of H on the surface occurs much faster than the desorption of H. In this case the surface phases which are present are in equilibrium with each other and μ_H is determined by the requirement that the chemical potential be the same in every phase. Define Θ_{av} to be the average density of H atoms present on the surface. For Θ_{av} equal to 1, the energy is minimized by complete coverage by the 2×1 monohydride phase. As Θ_{av} is increased from 1 to $\frac{4}{3}$, the additional H is incorporated by breaking Si-Si dimer bonds and forming dihydride units. To minimize the energy, according to the model, the added rows of dihydride should not be adjacent. Otherwise one incurs the energy cost of the repulsive interactions between neighboring dihydrides. Rows of dihydride can be added without creating any adjacent rows until the 3×1 phase covers the entire surface. Thus, for $1<\Theta_{av}<\frac{4}{3}$ the surface consists of a mixture of the 2×1 monohydride and 3×1 phases and μ_H is pinned at $\mu(2\times1|3\times1)$. Then as additional H is added to the surface and Θ_{av} increases beyond $\frac{4}{3}$, the chemical potential jumps to $\mu_H=\mu(3\times1|1\times1)$ as adjacent rows of dihydrides form to accommodate the additional H. Eventually, the 1×1 dihydride phase would cover the entire surface as Θ_{av} increases to 2.

The 1×1 phase observed experimentally following saturation exposures at temperatures less than 300 K is not well ordered. In fact, Chabal and Raghavachari[3] have argued that such a 1×1 phase is really a disordered 3×1

phase. In this case the observed 1×1 low-energy electron-diffraction pattern arises entirely from the bulk. On the other hand, the STM results of Boland[4] indicate that saturation exposures at room temperatures produces patches of the dihydride phase. At the same time significant disordering of the surface was observed. Cheng and Yates[16] observed SiH_4 production from a 1×1 surface in temperature programmed desorption experiments and have proposed that the SiH_4 originates from precursor SiH_3 groups present in the 1×1 phase. These latter two experimental results indicate that breaking of Si-Si backbonds is occurring concurrently with the formation of the dihydride phase.

Although a detailed investigation of the disorder in the 1×1 phase is beyond the scope of this work, a few remarks may be in order. It is likely that defects exist in the 1×1 phase which have a very low or perhaps a negative formation energy. Such defects could involve the formation of higher hydrides and would be stabilized if they permitted a reduction in the hydrogen-hydrogen repulsion. Since the formation of the 1×1 dihydride phase requires that $\mu_H \geq \mu(3\times1|1\times1)$, and since $\mu(3\times1|1\times1)$ is only 0.09 eV less than the chemical potential at which SiH_4 molecule formation becomes exothermic, it would not be surprising if defects involving adsorbed SiH_3 groups had very low formation energies. In general, the formation energy of defects involving higher hydrides will be reduced as μ_H increases. Thus, the 1×1 surface is more susceptible to defect formation than are the 3×1 and 2×1 surfaces.

In summary, the 3×1 monohydride plus dihydride structure proposed by Chabal and Raghavachari has been shown to be lower in energy than the 2×1 and 1×1 structures over a certain range of chemical potential. The relative stability of the 3×1 structure in this regime arises from repulsive interactions between H atoms in the 1×1 structure. These interactions stabilize the 1×1 canted-row dihydride structure with respect to the symmetric dihydride structure.

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