PHYSICAL REVIEW B VOLUME 57, NUMBER 11 15 MARCH 1998-I

Effect of hydrogen on the surface-energy anisotropy of diamond and silicon

Suklyun Hong* and M. Y. Chou†
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430

(Received 29 October 1997)

We have evaluated the surface free energies of hydrogen-covered (100), (111), and (110) surfaces of diamond and silicon as a function of the hydrogen chemical potential using first-principles methods. The change in surface-energy anisotropy and equilibrium crystal shape due to hydrogen adsorption is examined. The three low-index facets are affected differently by the presence of hydrogen and unexpected differences are found between diamond and silicon. Taking into account possible formation of local facets on the hydrogen-covered (100) surfaces, we find that the dihydride phase is not stable on both C(100) and Si(100), nor is the 3×1 phase on C(100). [S0163-1829(98)07208-7]

Adsorption of foreign atoms on a surface can significantly modify its physical and chemical properties. These adsorbates usually play an important role in thin-film growth by affecting, for instance, adatom diffusion and nucleation processes.[1–4] In some cases, the impurities act as a ''surfactant'' and greatly improve the morphology of the film. An example is in heteroepitaxial growth of semiconductors where the surfactant saturates the dangling bonds and thus lowers the surface free energy, leading to a floating layer segregated from the incorporated growing species.[5] In fact, adsorbate-induced changes in surface free energy have an interesting effect on surface morphology in general, as discovered by several recent experiments.[6–9] For instance, the equilibrium shape of small Ge pseudomorphic islands on Si(100) is found to depend strongly on the Sb (surfactant) coverage, and different types of facets form reversibly as the coverage is changed.[6] It is also found that the W(111) surface coated with about one monolayer (ML) of certain metals undergoes extensive restructuring to form microscopic facets after annealing.[7]

To our knowledge, adsorbate-induced changes in surface free energy and its anisotropy have not been examined in detail theoretically. Only one recent study has addressed hydrogen-induced reconstruction and faceting of Al surfaces.[10] On bare semiconductor surfaces, the surface energy is correlated with the number of dangling bonds on the ideal surface and the extent to which a reconstruction can reduce them. The surface-energy anisotropy can be considerably changed by the presence of foreign species if they form chemical bonds with surface atoms. In turn, the equilibrium shape of crystals covered by adsorbates can be different from that without adsorbates. In this paper, we investigate this effect using first-principles total energy calculations. We examine one of the most studied adsorption systems, namely, hydrogen on diamond and silicon, because of its technological importance. Hydrogen is a common impurity that plays a significant role in semiconductor growth,[3,11,12] a subject of vast interest. In addition, recent experiments find interesting results with unexpected differences between hydrogen covered silicon and diamond surfaces, which have not been understood. Adsorption of H during high-temperature Si(111) molecular beam homoepitaxy is found to change the growth mode and to cause film roughness:[8] the (111) planar area disappeared as other facets developed during growth in the presence of a continuous flux of atomic hydrogen. In contrast, etching of natural diamond by atomic hydrogen is found to be highly anisotropic with (111) facets forming irreversibly on both C(110) and C(100).[9]

Since surfaces of different orientations may adsorb different amounts of hydrogen and several adsorption phases with different coverages may occur on one single surface, we consider the surface in equilibrium with a hydrogen reservoir characterized by a hydrogen chemical potential.[13,14] Calculations we performed for hydrogen-covered (100), (110), and (111) diamond and silicon surfaces obtained the surface free energy as a function of hydrogen chemical potential at $T=0$. The ratio of surface free energies between these three low-index surfaces changed considerably upon hydrogen adsorption and noticeable differences between C and Si were found. Using these results, we will discuss the change in the equilibrium crystal shape when the surface is covered by hydrogen. We will also explain the development of different phases on the (100) surface, and discuss their stability against local facet formation.

The calculations were carried out using the pseudopotential method within the local-density-functional approximation. Plane waves up to an energy of 55 and 10 Ry were included to expand the wave functions in C and Si calculations, respectively. We generated soft Si and C potentials[15] from atomic ground states. The Si potentials have a cutoff radii of 1.90 a.u. and the p potential was chosen as the local potential. These gave a lattice constant of 5.42 Å and a bulk modulus of 0.940 Mbar, in agreement with the experimental values of 5.43 Å and 0.988 Mbar, respectively. Details of the C and H potentials and H/C(100) calculations are given elsewhere.[14] We used slabs of ten atomic layers separated by a vacuum region equal to six atomic layers. Atoms were fully relaxed with a residual force smaller than 0.01 or 0.005 Ry/a.u. For the Brillouin-zone integration we used a $6\times6\times2$ grid in the Monkhorst-Pack scheme for the 1×1 surface unit cell. For other periodicities, the number of points was scaled accordingly.

Among low-index diamond and silicon surfaces, the hydrogen-covered (100) surface exhibits the most interesting behavior. Three different phases have been observed on the

0163-1829/98/57(11)/6262(4)/$15.00

hydrogen-saturated Si(100) surface depending on experimental conditions:[16–18] (1) a 2×1 monohydride phase with hydrogen saturating remaining dangling bonds in the dimer reconstruction, (2) a 3×1 phase consisting of alternating monohydride and dihydride units with an ideal coverage of 1.33 ML, and (3) a bulklike 1×1 dihydride phase, poorly ordered. A pronounced H-atom etching was observed in the 1×1 phase, with (111) ledges surrounding the etched regions.[17] As for the C(100) surface, a stable 2×1 monohydride phase was found after hydrogen plasma treatment, but no 3×1 phase has ever been detected.[19,20] Küttel *et al.*[20] also reported that further exposure to atomic hydrogen destroyed the 2×1 phase and significantly increased the roughness of the surface.

We studied all three of the above phases on the (100) surface. The monohydride (1×1):H phase was considered on the (111) surface, as suggested by experiment.[21,22] It was found experimentally that bare C(110) did not reconstruct.[23] Therefore, we assumed that hydrogen simply saturated the single dangling bond on the surface atom (two per unit cell) to form a monohydride surface on C(110) and Si(110).

In order to compare surfaces with different hydrogen coverages, we consider the formation energy of each surface as a function of hydrogen chemical potential μ_H. The formation energy Ω is defined as[13]

$$\Omega = E + E_0 - n_Z\mu_Z - n_H\mu_H, \tag{1}$$

where E is the total energy of the surface system at zero temperature, E_0 the zero-point energy of hydrogen vibrations, and n_Z (Z=C, Si) and n_H the numbers of C, Si, and H atoms, respectively. We took $E_0 = n_H e_0$,[13] and estimated e_0, the zero-point energy per H, from the sum of vibrational frequencies of CH_4 and SiH_4. e_0 was set to 0.293 eV (Ref. 14) and 0.21 eV (Ref. 13) for H on C and Si, respectively. We used the bulk energy for μ_C and μ_{Si}. The range of hydrogen chemical potential μ_H is not unlimited. For example, if SiH_4 and CH_4 molecules can be formed from a reservoir of H and bulk Si and C with no cost of energy, respectively, the surface will be unstable to dissolution. Therefore, μ_H must be smaller than μ_H^0, the chemical potential which gives zero formation energy for SiH_4 or CH_4.[13] We calculated the value of μ_H^0 to be -15.49 eV for the C system and -14.48 eV for Si. In all the figures shown below, μ_H is measured relative to μ_H^0.

The surface energy γ associated with the hydrogen-covered surface is then taken as the formation energy in Eq. (1) divided by the surface area. The results for three low-index diamond and silicon surfaces as a function of μ_H^* $(\equiv \mu_H - \mu_H^0)$, are shown in Fig. 1. Only the most stable phase at a given chemical potential is plotted for each orientation. Therefore, the curves are piecewise linear; the slope changes (denoted by open symbols) when a change in the lowest-energy phase occurs on one surface. If the hydrogen chemical potential is too low, adsorption is not energetically favorable and the bare surface has the lowest formation energy. This is represented by the horizontal lines toward the left of the figure, which give the surface energies of bare surfaces. The calculated $T=0$ values for (111), (100), and (110) surface energies are 4.12, 5.60, and 5.96 J/m^2 for C, and 1.45, 1.51, and 1.99 J/m^2 for Si, respectively.[25] For bare Si surfaces, the calculated ratios $\gamma(100)/\gamma(111)$ and $\gamma(110)/\gamma(111)$ are 1.04 and 1.38, respectively. In a measurement of the equilibrium shape of small voids in Si these two ratios were found to be 1.11 and 1.16.[26] Since the unreconstructed and relaxed structure was considered in the calculation for Si(110), it is possible that the calculated (110) energy is higher than what it should be.

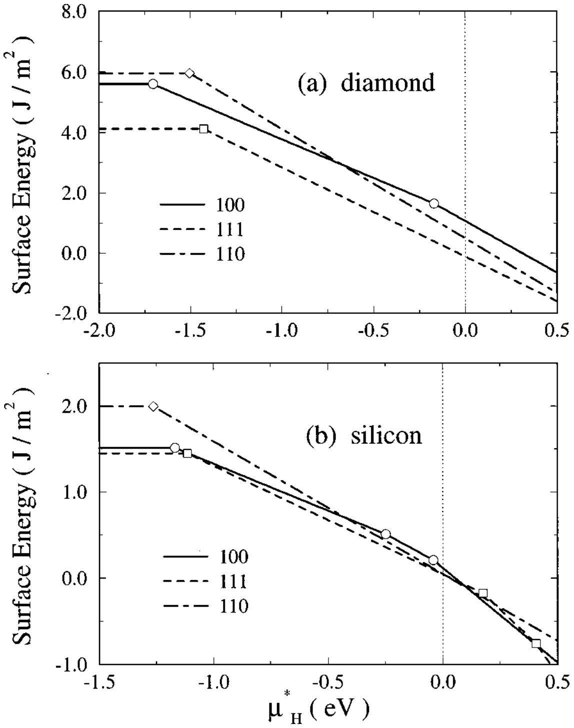

FIG. 1. Surface free energies [Ω in Eq. (1) divided by area], of the (100), (111), and (110) surfaces for (a) diamond and (b) silicon as a function of hydrogen chemical potential $\mu_H^* (\equiv \mu_H - \mu_H^0)$ at $T=0$. The open symbols represent locations of phase changes on each surface. μ_H^0 is the hydrogen chemical potential at which the formation energy of CH_4 or SiH_4 is zero. See text for details.

With increasing hydrogen chemical potential, the curves enter the monohydride phase after a slope change. This happens on (100), (111), and (110) surfaces at μ_H^* values of -1.70, -1.43, and -1.50 eV for C, and -1.17, -1.11, -1.26 eV for Si, respectively. The Si (100) curve [Fig. 1(b)] further changes its slope with increasing μ_H^*, first going into the (3×1):1.33H phase at $\mu_H^* = -0.25$ eV and then the (1×1):2H (canted) phase at $\mu_H^* = -0.04$ eV. These phase boundaries (open circles) agree well with the results of -0.24 and -0.09 eV in Ref. 13. The C (100) curve [Fig. 1(a)] only has a small (3×1):1.33H region associated with negative μ_H^*. The (1×1) region (not shown) is further on the right with positive μ_H^*, out of the region of interest.[14]

For completeness, we also checked the three-dangling-bond (3DB) (111) structures discussed by Kern *et al.*,[24] who suggested that 3DB (2×1):2H and 3DB (1×1):3H phases on C(111) can be stabilized at high hydrogen chemical potential. The relevant chemical potential is about 2 eV higher than μ_H^0 for carbon, therefore out of the region of interest. For Si(111) these phases are also located at positive μ_H^*, with phase boundaries at $\mu_H^* = 0.18$ and 0.41 eV, respectively.

The main results from Fig. 1 are (i) the (111) surface (bare or covered by hydrogen) is lowest in energy in most of the chemical potential range of interest (namely, $\mu_{\rm H}^{*}<0$). This is especially significant for C, where $\gamma(111)$ is much lower than the other two curves in Fig. 1(a). For Si, however, regions exist where other surfaces are close in energy. [Note the energy scale change in Fig. 1(b) compared with Fig. 1(a).] (ii) Upon hydrogen adsorption, the ratio $\gamma(100)/\gamma(111)$ increases with $\mu_{\rm H}^{*}$ because of a difference in hydrogen density on these two surfaces. For the monohydride phase, each 1×1 surface unit cell has one hydrogen atom. The (100) surface has a larger unit cell area, thus a smaller density. When the ratio $\gamma(100)/\gamma(111)$ reaches $\sqrt{3}$ at $\mu_{\rm H}^{*}\approx-0.55$ and -0.10 eV for C and Si, respectively, the {100} facet will disappear, according to the Wulff construction. (iii) In contrast, the ratio $\gamma(110)/\gamma(111)$ decreases with $\mu_{\rm H}^{*}$ upon hydrogen adsorption for the same reason. As a result, $\gamma(100)$ and $\gamma(110)$ change order at certain points. According to the Wulff construction, the bare (110) surface does not appear as a facet on the equilibrium crystal shape because it is an outward cusp,[26] but with hydrogen adsorption it may become a stable facet for Si at $\mu_{\rm H}^{*}\approx-1.12$ eV. However, this does not happen for C because $\gamma(111)$ remains sufficiently low.

Based on the above results, we conclude that the {111} facet dominates on hydrogen-covered C surfaces. This provides an explanation, based on energetics, for the formation of {111}-oriented facets on C(110) and C(100) in the presence of atomic hydrogen.[9] Previously this etching anisotropy by atomic hydrogen was attributed to kinetic effects.[9] On the other hand, the {111} facet is much less dominating on hydrogen-covered Si surfaces. The calculation showed that even the {110} facet can possibly be stabilized upon hydrogen adsorption. It is then not surprising that Hoegen *et al.* observed the disappearance of planar (111) areas and the formation of facets with orientations ranging from 113 to 779 during Si(111) molecular bean homoepitaxy under continuous H flux.[8]

The fact that the ratio $\gamma(100)/\gamma(111)$ increases with $\mu_{\rm H}$ may also affect surface stability of hydrogen-covered (100) thin films against local facet formation. Since any local facet formation increases the surface area, the energy associated with forming hydrogen-covered (111) and (110) facets is taken from the individual surface energy in Fig. 1, multiplied by the area enhancing factor $\sqrt{3}$ and $\sqrt{2}$, respectively. They correspond to monohydride (111) and (110) facets, and have the same slope as the (100) dihydride phase. Here we have neglected any edge energy to examine the trend. Plotted in Fig. 2 are the formation energies of various phases on the (100) surface, together with the energy of forming (111) and (110) facets, as a function of $\mu_{\rm H}^{*}$ for (a) C and (b) Si.

We focus on the region where competition between (111) and (110) facets and $n\times1$ phases of the (100) surface occurs. In both C and Si, these scaled facet formation energies are below the parallel curve for the $(1\times1){:}2$H (canted) phase. Therefore, the (1×1) dihydride phase, if it exists, will be highly subject to facet formation, leading to a rough surface. This may be the reason why stable, well-ordered dihydride phase has never been observed on either C(100) or Si(100).

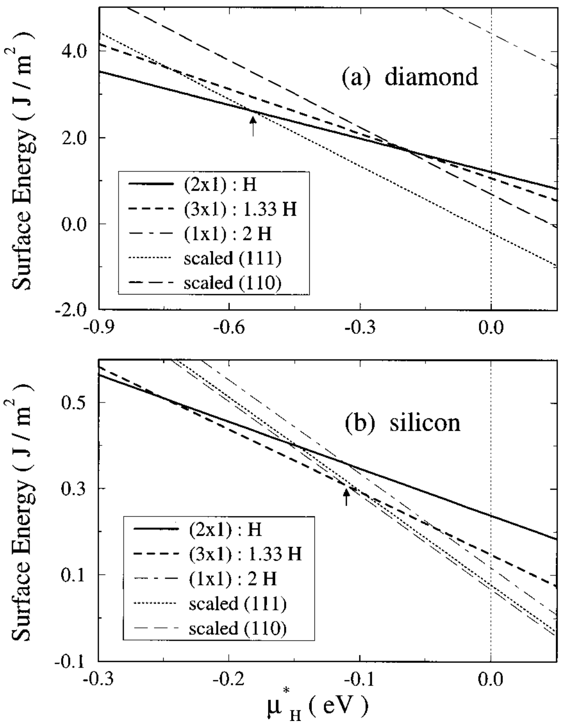

FIG. 2. Formation energy per unit area for various phases of hydrogen-covered (a) C(100) and (b) Si(100) surfaces as a function of hydrogen chemical potential $\mu_{\rm H}^{*}$. The scaled energies of (111) and (110) facets are also shown.

The possibility of facet formation also affects stability of the $(3\times1){:}1.33$H phase on C(100). As shown in Fig. 2(a), the dotted line corresponding to the energy of the (111) facet intersects with that of the 2×1 monohydride phase at around $\mu_{\rm H}^{*}=-0.55$ eV (arrow). Previously[14] we found a very small region of the 3×1 phase (about 10% of the stable region of 2×1) to be stable, namely, with a negative $\mu_{\rm H}^{*}$. Now the 3×1 curve is completely above those of ideal (111) and (110) facets. This may eliminate the possibility of having a stable $(3\times1){:}1.33$H phase and explain why it has never been observed on C(100). Also, huge morphological change and surface roughness upon hydrogen exposure observed by Küttel *et al.*[20] may be explained by the (local) facet formation.

On the other hand, the Si(100) result is quite different. In Fig. 2(b), the (111) and (110) facet energy lines are close and intersect the (3×1) phase region at about -0.1 eV (arrow). As a result, the stable region of the (3×1) phase is reduced to -0.25 eV $<\mu_{\rm H}^{*}<-0.1$ eV, but not eliminated as in the C(100) case. This is consistent with the fact that the 3×1 phase can be created under specific experimental conditions.[16–18]

In conclusion, we have calculated the surface energies of hydrogen-covered (100), (111), and (110) surfaces of diamond and silicon from first principles as a function of hydrogen chemical potential at $T=0$. It is found that hydrogen adsorption has a significant effect on surface energy anisotropy, a delicate balance between different bindings and adsorbate density. The bare and hydrogen-covered C(111) surfaces distinctly have the lowest surface energy over the whole hydrogen chemical potential range of interest, while Si(111) can be close in energy to Si(110) and Si(100) in some chemical potential range. The ratio $\gamma(100)/\gamma(111)$ increases with the hydrogen chemical potential. As a result, the $\{100\}$ facet can disappear at certain values of the hydrogen chemical potential. On the other hand, the $\{110\}$ facet, which does not appear in the equilibrium crystal shape of bare surfaces, can be stabilized by hydrogen adsorption on Si, but not on C. The possibility of forming local $\{111\}$ facets on the hydrogen-covered (100) surface considerably affects stability of various ordered phases, causing the 1×1 dihydride phase to be highly unstable. It also affects the (3×1):1.33H phase, reducing its stable region on Si(100), while suppressing it completely on C(100).

We thank Dr. John Northrup for helpful discussions and Dr. Andrew Zangwill for a critical reading of the manuscript. This work was supported in part by the National Science Foundation (Grant No. DMR-9157537), the Department of Energy (Grant No. DE-FG02-97ER45632), and the National Energy Research Scientific Computing Center (NERSC). M.Y.C. thanks the Packard Foundation for its support.

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[*] Present address: Oak Ridge National Laboratory, Oak Ridge, TN 37831-6114. Electronic address: hongs@ornl.gov

[†] Electronic address: meiyin.chou@physics.gatech.edu

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[25] The surface energies of bare C(111) and Si(111) were calculated for the 2×1 π-bonded chain structure. A correction of 60 meV per 1×1 cell was then included for Si(111) to account for the energy difference between the 2×1 and 7×7 structures [K. D. Brommer *et al.*, Phys. Rev. Lett. **68**, 1355 (1992)]. The 2×1 symmetric dimer structure was considered for C(100) and the $c(4\times2)$ structure for Si(100), respectively. The unreconstructed and relaxed structures were considered for both C(110) and Si(110).

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