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Si(001) $c(4\times2)$–$p(2\times2)$ surface phase transitions induced by electric fields and doping

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Abstract

Density functional calculations on the relative stability of $c(4\times2)$ and $p(2\times2)$ reconstructed Si(001) surfaces exposed to external electric fields and charge injection are presented. Electric fields parallel to the [001] direction or electrons inserted into surface states are found to favor the $p(2\times2)$ over the $c(4\times2)$ reconstruction. This explains recent experimental findings for Si and Ge(001).

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Keywords: Density functional theory; Silicon surface; Scanning tunneling microscopy; Phase transition

Clean Si(001) surfaces reconstruct due to the dimerization of the topmost atoms. The dimers are asymmetric, consisting of a sp^2-like bonded "down" atom, which moves closer to the plane of its three nearest neighbors, and an "up" atom, which moves away from the plane of its neighbors and possesses a s-like dangling bond. The buckling of the Si dimers alternates within the dimer row. Depending on the registry of buckling in neighboring dimer rows, $c(4\times2)$ and $p(2\times2)$ reconstructions may form. The demonstration of phase manipulation between these reconstructions at temperatures below 40 K using the scanning tunneling microscope (STM) [1–3] is perhaps one of the most interesting recent findings of surface science. The dimers are found to prefer the $p(2\times2)$ ordered phase when scanned with a negative tip. Applying a voltage pulse or scanning with a positive tip tends to reverse $p(2\times2)$–$c(4\times2)$. Similar experiments have been performed on Ge(001) surfaces [4,5]. Here a phase transition with hysteresis between $c(4\times2)$ and $p(2\times2)$ surface reconstructions was induced by the STM bias below 80 K. The physical mechanism behind the STM induced change of surface reconstruction is not understood. Sagisaka et al. [3] assume electron injection into the surface to be responsible whereas Takagi and co-workers [4] proposed strain effects due to the applied external field. The understanding of the experimental findings is further complicated by the influence of surface defects on the phase transition [6].

Here we present *first-principles* calculations on the energetics of the Si(001) surface in the presence of external electric fields parallel to the surface normal as well as upon charge injection. The Vienna ab initio simulation package (VASP) implementation [7] of the gradient-corrected [8] density functional theory (DFT–GGA) is used for the electronic-structure and total-energy calculations. The electron–ion interaction is described by non-normconserving ultrasoft pseudopotentials [9]. The Si(001) surface is modeled with a supercell containing eight atomic Si layers and a vacuum region equivalent in thickness to 12 atomic layers. The bottom of the Si slab is hydrogen saturated and kept frozen during the structure optimization. The external electric field E_z is modeled by adding a saw-tooth potential along the surface normal to the external potential entering the Kohn–Sham equation. We define a positive electric field to be parallel to the surface normal, i.e., the [001]

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direction. That corresponds to STM measurements applying a negatively biased tip. Assuming a typical tip-sample distance of 1 nm, a bias voltage of +1.0 V corresponds to a strong electric field of 0.1 V/Å. In our study, we simulated electric fields ranging from −0.2 to 0.2 V/Å. Fig. 1 shows the planarly averaged effective electron potential for different fields along the [0 0 1] direction after electronic self-consistence is reached. As expected, the strong gradient of the effective potential in the vacuum region is strongly reduced in the region of the Si bulk material, because of the screening.

The starting point for the calculation is the relaxation of the "unperturbed" Si(0 0 1) surface, enforcing $p(2\times2)$ or $c(4\times2)$ symmetry, respectively. We calculate a Si dimer length of 2.35 Å for both reconstructions and determine a buckling of 0.753 Å and 0.750 Å, respectively, for the $c(4\times2)$ and $p(2\times2)$ structures. The arrangement of dimers in $c(4\times2)$ symmetry is energetically slightly preferred compared to the $p(2\times2)$ symmetry, by 0.7 meV per dimer. Our findings corroborate earlier theoretical results, see, e.g., Refs. [10–13]. The lateral symmetry of the dimer arrangement is governed by electrostatic interactions between the asymmetric dimers and the minimization of the dimer buckling induced strain energy. Assuming a charge transfer of about 0.1 electrons from the "down" to "up" atoms one finds that electrostatics favors the $p(2\times2)$ over the $c(4\times2)$ symmetry by an energy difference of the order of a few meV/dimer [14]. This indicates that the overall energetic preference of the $c(4\times2)$ structure is not due to electrostatics, but must be related to the better accommodation of surface strain. This hypothesis is corroborated by the slightly more pronounced dimer buckling in case of the $c(4\times2)$ symmetry.

The difference between the surface energies of $p(2\times2)$ and $c(4\times2)$ reconstructed Si(0 0 1) versus the applied external field is shown in Fig. 2. In agreement with the STM measurements [1–3], positive electric fields favor the $p(2\times2)$ over the $c(4\times2)$ symmetry. This can be understood from the response of the slightly negatively (positively) charged "up" ("down") Si dimer atoms to the external field, as shown in the inset of Fig. 2. Positive (negative) electric fields lead to a decrease (increase) of the dimer buckling: The vertical shear between the two dimer atoms changes by about 0.005 Å, if exposed to an electric field of 0.2 V/Å along the surface normal. The strain resulting from the tilting of the surface dimers can be accommodated better in a $c(4\times2)$ compared to a $p(2\times2)$ symmetry, as concluded above from the energetics of the surface in the absence of external fields. Positive (negative) electric fields thus weaken (strengthen) the relative influence of strain on the delicate energy balance of the Si(0 0 1) surface. Because the dipole–dipole interaction favors the $p(2\times2)$ arrangement of the Si dimers, this symmetry is preferred upon application of positive fields. It is interesting to note that the response of the surface charge density alone, i.e., assuming the atomic coordinates to be frozen, would lead to an opposite behavior: The field induced redistribution of electrons favors $p(2\times2)$ and $c(4\times2)$ reconstructions for negative and positive fields, respectively [15].

Apart from static electric fields, STM experiments may lead to local charging effects on the time scale of the carrier lifetimes, additionally affecting the surface energetics. Mitsui and Takayanagi [16] interpret their STM results in terms of a lateral spread of injected electrons over the surface states. There are further experimental hints for a relation between the occupation of surface states and the surface energetics: Hata et al. [17] observed $p(2\times2)$ surface reconstructions exclusively on n-type substrates. Due to the

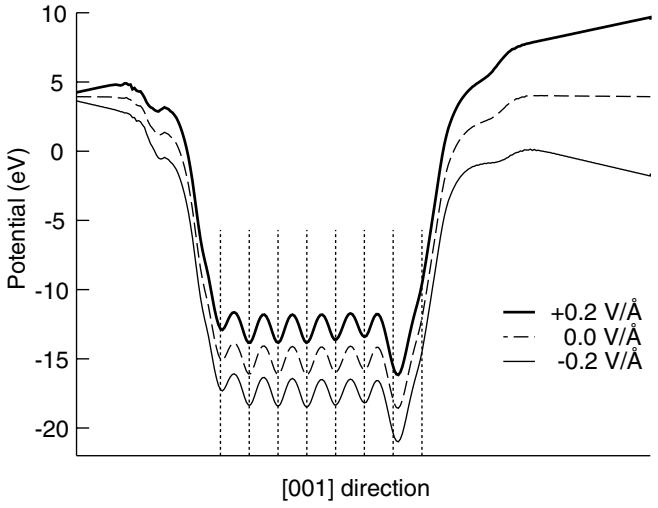

Fig. 1. Planarly averaged effective electron potential along the [0 0 1] direction for different external fields. The positions of the atomic layers are indicated by dashed lines.

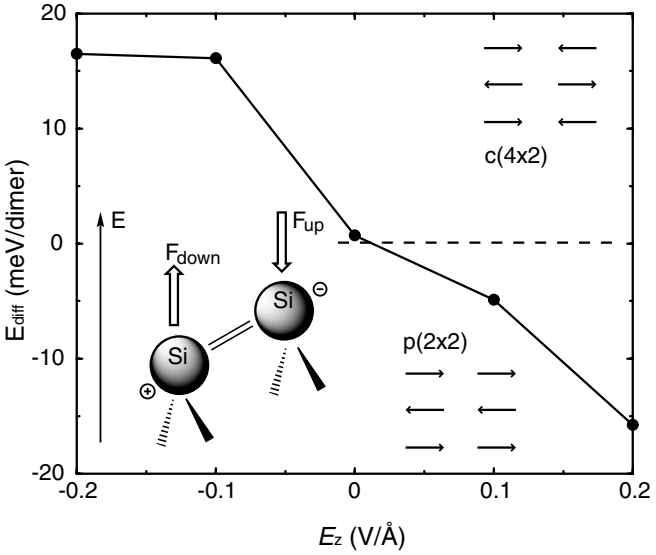

Fig. 2. Energy difference $E_{diff} = E_{p(2\times2)} - E_{c(4\times2)}$ in dependence on external fields along the surface normal. The insets indicate the dimer orientation of the Si(0 0 1) surface reconstructions and the forces acting on the "up" and "down" Si dimer atoms in the presence of a positive electric field.

existence of acceptor-like surface states about 0.5 eV above the bulk valence band maximum, an excess of negative charge may occur at the surface of n-type substrates [18]. It has also been discussed that electron irradiation onto the surface during electron diffraction experiments is causing partial surface phase transitions from $c(4\times2)$ to $p(2\times2)$, leading to a disordered surface [2,3,19,20].

In order to study the possibility of such an effect, we performed total-energy calculations on surfaces which are slightly negatively or positively charged, with a charge variation α ranging from $-0.2e$ to $0.2e$ for the $p(4\times2)$ surface unit cell. The excess charge is compensated by a constant charge background. The influence of the excess charge on the surface energetics is shown in Fig. 3. The injection of electrons stabilizes the $p(2\times2)$ surface reconstruction, whereas the influence of additional holes is small. In contrast to the case of an applied external field, the influence of the atomic relaxations on the change of the surface energetics is negligible. The preference of the $p(2\times2)$ symmetry upon electron injection is determined by electronic effects. The charge density difference between the electron-injected ($0.2e$) and neutral surface is shown in the inset of Fig. 3. As can be seen, the additional charge is mainly localized above the surface, on both Si dimer atoms, but has a slightly larger probability to be localized at the "up" atom, thus increasing the surface dipole. The injection of electrons thus enhances the dipole–dipole interaction and leads therefore to the energetic preference of the $p(2\times2)$ reconstructed surface. The injection of holes, in contrast, barely alters the dimer related surface dipoles, because additional holes are less surface localized than additional electrons.

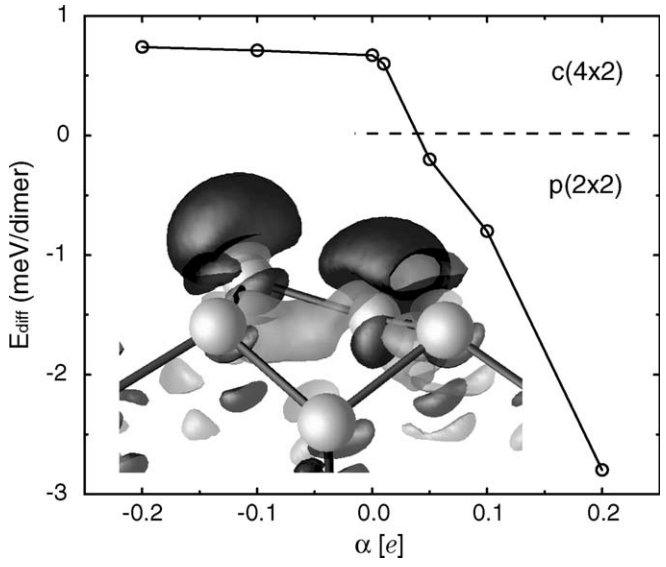

Fig. 3. Energy difference $E_{\mathrm{diff}} = E_{p(2\times2)} - E_{c(4\times2)}$ in dependence on the surface charging. The inset shows the calculated charge density difference upon injection of 0.2 electrons into the surface slab. Dark and light isosurfaces ($\pm1\times10^{-3}\ e/\text{Å}^3$) represent charge accumulation and depletion regions, respectively.

In conclusion, we performed ab initio total-energy and electronic structure calculations for the Si(001) surface. In agreement with previous *first-principles* calculations, we find that asymmetric dimers arranged in $c(4\times2)$ symmetry represent the surface ground state. However, two mechanisms may shift the delicate surface energy balance: (i) external electric fields along the surface normal reduce the dimer buckling and thus the surface strain and (ii) electrons injected into the surface enhance the dipole–dipole interaction. Both an enhanced dipole–dipole interaction as well as reduced surface strain favor the $p(2\times2)$ reconstruction and may thus lead to a phase transition. The computational findings thus explain a series of recent low-temperature STM studies on the structure of (001) surfaces of Si and Ge. The origin of the temperature dependence of the phase manipulation feasibility as well as the influence of defects still remain open questions, however.

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