Energetics of Si(001) Surfaces Exposed to Electric Fields and Charge Injection

K. Seino,* W. G. Schmidt, and F. Bechstedt
Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität, Max-Wien-Platz 1, 07743 Jena, Germany
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We perform density-functional calculations on the influence of external electric fields and electrons or holes injected into surface states on the relative stability of $c(4 \times 2)$ and $p(2 \times 2)$ reconstructed Si(001) surfaces. It is shown that an electric field parallel to the [001] direction or the insertion of electrons into surface states favors the formation of $p(2 \times 2)$ periodicities. Our results explain recent experimental studies reporting changes of surface reconstruction of Si and Ge(001) surfaces induced by the scanning tunneling microscope and the occurrence of $p(2 \times 2)$ reconstructions on (001) surfaces of n-doped Si.

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There has been a long-standing interest in the atomic and electronic structures of the Si(001) surface (see, e.g., Refs. [1,2]), due to its numerous industrial applications and its model character for semiconductor surface science. Until recently, its local geometrical features and the nature of the reconstruction were considered to be well understood: Clean (001) surfaces of Si (and Ge) reconstruct due to the dimerization of the topmost atoms. The dimers are asymmetric, consisting of an 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 an s-like dangling bond. The process of rehybridization is accompanied by a charge transfer from the down to the up atom. To minimize the electrostatic energy and to relieve local stress, the direction of buckling alternates within the dimer rows. The registry of buckling in neighboring dimer rows is phase shifted, such that the Si(001) surface ground state reconstructs $c(4 \times 2)$ [2]. That picture has been supported by a large number of first-principles calculations (see, e.g., Ref. [3]) which find the $c(4 \times 2)$ structure to be slightly favored (of the order of meV/dimer) over the $p(2 \times 2)$ structure, where the buckling in neighboring dimer rows occurs in phase (cf. Fig. 1).

Recently, however, the atomic configuration of the Si(001) surface at very low temperatures has become a subject of debate. That concerns, on the one hand, the question whether the true surface ground state features symmetric or asymmetric dimers. However, there seems to be some experimental [4–9] and theoretical [10,11] evidence that the observation of symmetric dimers at very low temperature [4,12] does not necessarily imply that symmetric dimers correspond to the surface ground state. On the other hand, phase manipulation between $c(4 \times 2)$ and $p(2 \times 2)$ has been performed at 4.2 K, using the scanning tunneling microscope (STM) [13]. The dimers were found to prefer the $p(2 \times 2)$ ordered phase when scanned with a negative tip. Applying a voltage pulse or scanning with a positive tip tends to reverse $p(2 \times 2)$ to $c(4 \times 2)$. Similar experiments have also been performed on Ge(001) surfaces [14,15]. Here a phase transition with hysteresis between $c(4 \times 2)$ and $p(2 \times 2)$ surface reconstructions was induced by controlling the STM bias voltage below 80 K. These experiments have been discussed in the context of realizing a rewritable nanometer-scale memory [16,17]. The physical mechanism behind the STM induced change of surface reconstruction, however, is not understood. Local steric and electronic interactions between tip and sample [17–19] are most likely not sufficient to explain the findings, because they can hardly account for the bias and current dependent size of the affected surface area [15].

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 electron or hole injection into surface states. These external factors are found to influence the subtle energy balance between electrostatics and local strain at the surface, effectively favoring the formation of $p(2 \times 2)$ reconstructed domains for certain conditions. This may explain the experimentally observed possibility of switching between different surface reconstructions [13–15].

Total-energy and electronic-structure calculations are performed using the Vienna Ab-initio Simulation Package (VASP) implementation [20] of the generalized gradient approximation corrected [21] density functional

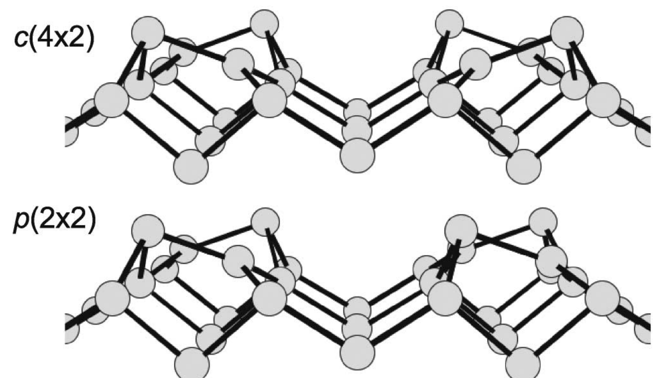

FIG. 1. Perspective view of the $c(4 \times 2)$ and $p(2 \times 2)$ reconstructed Si(001) surfaces.

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theory. The electron-ion interaction is described by non-norm-conserving ultrasoft pseudopotentials [22,23]. The valence wave functions are expanded into plane waves up to an energy cutoff of 20 Ry. The Brillouin zone integrations are performed using sets corresponding to 64 **k** points in the full (1×1) surface Brillouin zone. All calculations are performed using the calculated Si equilibrium lattice constant of 5.456 Å.

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 $\mathcal{E}_z$ is modeled by adding a sawtooth 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] 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.

The starting point for our calculation was the relaxation of the "unperturbed" Si(001) surface, enforcing $p(2 \times 2)$ or $c(4 \times 2)$ symmetry, respectively. We calculate a Si dimer length of 2.35 Å for both reconstructions and determine buckling angles of 18.7° and 18.6°, respectively, for the $c(4 \times 2)$ and $p(2 \times 2)$ structures. The arrangement of dimers in $c(4 \times 2)$ symmetry is energetically slightly preferred compared to the $p(2 \times 2)$ symmetry, by 0.7 meV per dimer. Our findings corroborate earlier theoretical results; see, e.g., Ref. [3].

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 the up atom (as concluded from core-level spectroscopy [24]), one finds that electrostatics favors the $p(2 \times 2)$ over the $c(4 \times 2)$ symmetry by an energy difference of the order of a few meV/dimer [25]. This indicates that the overall energetic preference of the $c(4 \times 2)$ 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 $c(4 \times 2)$ symmetry.

In order to study the influence of an external electric field on the surface energetics we first varied the field from −0.2 to 0.2 V/Å, keeping the atomic coordinates of the $c(4 \times 2)$ and $p(2 \times 2)$ surfaces frozen. As can be seen in Fig. 2, positive (negative) fields lead to an energetic preference of $c(4 \times 2)$ ($p(2 \times 2)$) reconstructed domains. The energy difference $E_{\mathrm{diff}} = E_{p(2\times2)} - E_{c(4\times2)}$ depends linearly on the electric field. In a second step we allowed both the electronic wave functions and the atoms to respond to the external field. The results (cf. Fig. 2) now

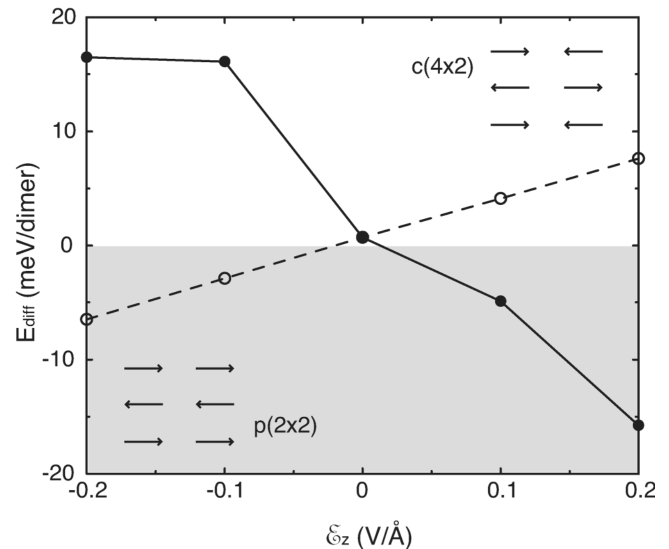

FIG. 2. Energy difference $E_{\mathrm{diff}} = E_{p(2\times2)} - E_{c(4\times2)}$ in dependence on external fields along the surface normal. Open and solid circles represent values for frozen and relaxed surface geometries, respectively. The insets indicate the dimer orientations of Si(001) surface reconstructions.

show a reversal of the trend calculated for frozen surface configurations: Positive electric fields favor the $p(2 \times 2)$ over the $c(4 \times 2)$ symmetry, in agreement with the STM measurements [13].

To better understand these findings we analyze the influence of external electric fields on the surface charge density and structural relaxation. A positive or negative external electric field leads to a charge transfer from the uppermost surface atoms towards the bulk or vice versa, respectively. This is shown in Fig. 3, where we have plotted the difference of the charge densities calculated for surfaces exposed to positive and zero electric fields. As can be seen, in particular, the charge at the up atom has been reduced due to the application of the positive field. The overall charge transfer caused by a field along

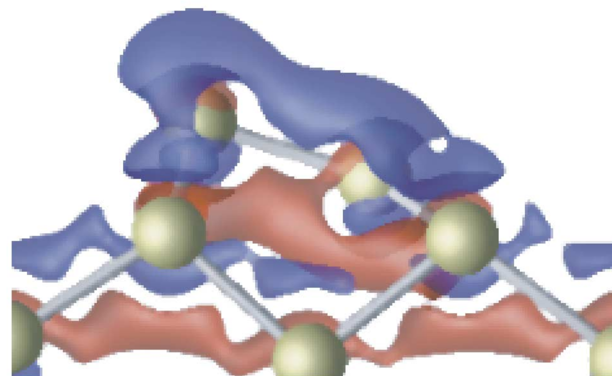

FIG. 3 (color online). Calculated charge density difference induced by an electric field $\mathcal{E}_z = 0.2$ V/Å. Red (light gray) and blue (dark gray) isosurfaces ($\pm 0.08e/\text{Å}^3$) represent charge accumulation and depletion regions, respectively.

the surface normal also changes the lateral charge distribution, affecting the strengths of the dipoles formed by the Si surface dimers. Positive (negative) electric fields weaken (strengthen) the dipoles formed between the negatively charged up and the positively charged down atoms of the Si surface dimers: For relaxed geometries we calculate dipole changes of -1.33 and 0.75 D upon application of an external field of 0.2 and -0.2 V/Å, respectively. The electrostatic dipole-dipole interaction of the Si dimers favors the $p(2 \times 2)$ symmetry, as discussed above. The enhancement (suppression) of the dimer dipoles upon application of a negative (positive) electric field thus favors the $p(2 \times 2)$ ($c(4 \times 2)$) symmetry, if no strain effects are considered. This is in agreement with the *ab initio* results obtained for *frozen* geometries.

However, external electric fields do not affect only the charge distribution at the surface, but also the equilibrium positions of the surface atoms. Key structural parameters after the ionic relaxation for different field strengths are compiled in Table I. Negative (positive) electric fields lead to lengthening (shortening) of the Si surface dimer and an increase (decrease) of the dimer tilting. This is simply the response of the slightly negatively (positively) charged up (down) Si dimer atoms to the external field. The strain resulting from the tilting of the surface dimers can be accommodated better in a $c(4 \times 2)$ compared to a $p(2 \times 2)$ symmetry, as concluded above from the energetics of the surface in the absence of external fields. This effect overcompensates the opposite trend from electrostatics and explains why negative electric fields favor the formation of $c(4 \times 2)$ reconstructed Si surfaces. Similar arguments have been suggested in Ref. [14] on the basis of STM measurements on Ge(001).

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 interpret their STM results in terms of a lateral spread of injected electrons over the surface states [5]. There are further experimental hints for a relation between the occupation of surface states and the surface energetics: Hata *et al.* [7] observed $p(2 \times 2)$ surface reconstructions exclusively on n-type substrates. Because of the existence of acceptorlike 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 [26].

TABLE I. Key structural parameters of Si(001) surfaces with and without external electric fields: d_D, φ, and d_h denote the Si dimer length, buckling angle, and vertical shear.

	$\mathcal{E}_z$ (V/Å)	d_D (Å)	φ (°)	d_h (Å)
$p(2 \times 2)$	-0.2	2.36	18.62	0.754
	0.0	2.35	18.58	0.750
	0.2	2.34	18.56	0.746
$c(4 \times 2)$	-0.2	2.36	18.71	0.758
	0.0	2.35	18.65	0.753
	0.2	2.34	18.63	0.748

We studied the influence of electrons or holes injected into surface states by performing total-energy calculations on slabs that are slightly negatively or positively charged, with a charge variation α ranging from $-0.2e$ to $0.2e$ for the (4×2) surface unit cell. The excess charge is compensated by a smeared background charge of appropriate sign. The charge density difference between the electron-injected ($0.2e$) and neutral surfaces is shown in Fig. 4. 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 calculated influence of the charging on the surface energetics is plotted in Fig. 5. The injection of electrons (holes) stabilizes the $p(2 \times 2)$ ($c(4 \times 2)$) surface reconstruction. We find the influence of additional electrons on the surface energetics to be much more pronounced than the influence of holes, which barely alter the total-energy results for the charging values considered here. To investigate the origin of the changed surface energetics we performed separate calculation with and without structural relaxation. The influence of the atomic relaxations on the change of the surface energetics is negligible (see Fig. 5). The preference of the $p(2 \times 2)$ symmetry upon electron injection is determined by electronic effects. The electrostatic dipole-dipole interaction favors the $p(2 \times 2)$ over the $c(4 \times 2)$ symmetry. The enhancement of the dimer related dipole strength upon injection of electrons will thus lead to the energetical preference of $p(2 \times 2)$ reconstructed surfaces. In contrast, the injection of holes barely alters the dimer related surface dipoles. According to our calculation, the hole induced dipole change is nearly 5 times smaller than that calculated for surface injected electrons. This is related to the partial

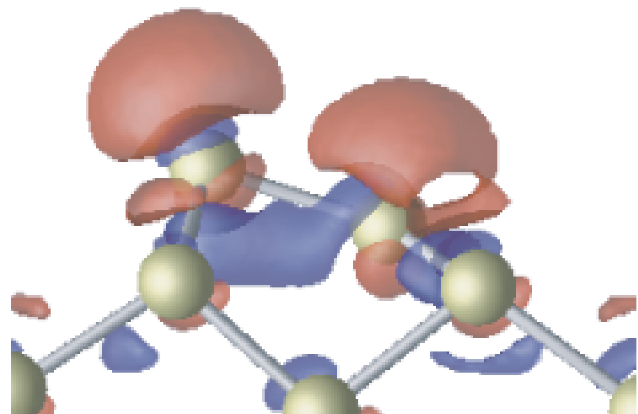

FIG. 4 (color online). Calculated charge density difference upon injection of 0.2 electrons into the surface slab. Red (light gray) and blue (dark gray) isosurfaces ($\pm 1 \times 10^{-3} e/\text{Å}^3$) represent charge accumulation and depletion regions, respectively.

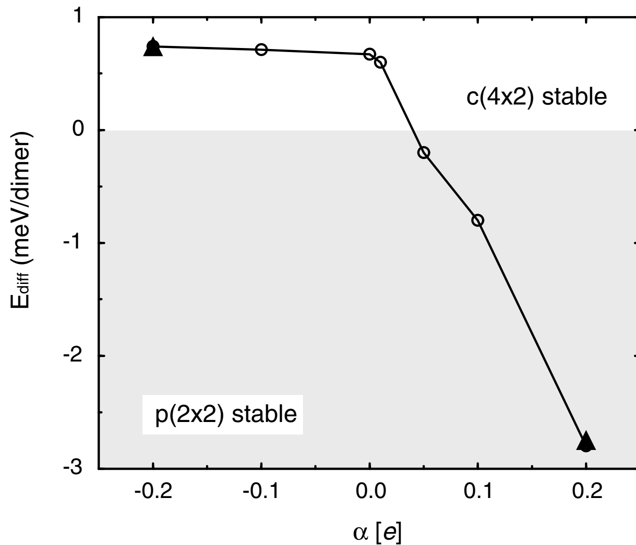

FIG. 5. Energy difference $E_{\rm diff} = E_{p(2\times2)} - E_{c(4\times2)}$ in dependence on the surface charging. Circles and triangles represent the values obtained for frozen and relaxed surface geometries, respectively.

degeneracy of the occupied Si(001) surface states with bulk states, which leads to a stronger delocalization of the holes. Their influence on the surface energetics is therefore small.

In conclusion, we performed *ab initio* total-energy and atomic structure calculations for the Si(001) surface. In agreement with the vast majority of previous *first-principles* calculations, we find that asymmetric dimers arranged in $c(4 \times 2)$ symmetry represent the surface ground state. However, we identified two mechanisms that shift the energy balance in favor of the formation of $p(2 \times 2)$ reconstructions: (i) external electric fields pointing along the surface normal and (ii) electrons inserted into surface states. Our findings provide a natural explanation of a series of recent low-temperature STM studies on the structure of (001) surfaces of Si and Ge. Similar effects may be expected at further surfaces that are characterized by a delicate balance between electronic and strain energy.

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*Electronic address: seino@ifto.physik.uni-jena.de

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