Te covered Si(001): a variable surface reconstruction

Prasenjit Sen(1), S. Ciraci(1,2), Inder P. Batra(1), and C. H. Grein(1)
(1) Department of Physics, University of Illinois at Chicago, Chicago, IL 60607-7059
(2) Department of Physics, Bilkent University, Bilkent, Ankara, 06533 Turkey

At a given temperature, clean and adatom covered silicon surfaces usually exhibit well-defined reconstruction patterns. Our finite temperature ab-initio molecular dynamics calculations show that the tellurium covered Si(001) surface is an exception. Soft longitudinal modes of surface phonons due to the strongly anharmonic potential of the bridged tellurium atoms prevent the reconstruction structure from attaining any permanent, two-dimensional periodic geometry. This explains why experiments attempting to find a definite model for the reconstruction have reached conflicting conclusions.

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Relaxation and reconstruction of clean and adatom covered surfaces is an active field of study. Tremendous efforts have been devoted to observing and understanding how the symmetry and atomic configurations of surfaces change, and how these changes affect the chemical and physical properties of surfaces. Particular atomic structures with well-defined reconstruction geometry are verified and sometimes predicted, by performing static total energy calculations at T = 0 K. Atomic configurations corresponding to the global or local minima on a Born-Oppenheimer surface are then attributed to stable surface structures.

In an effort to promote technology by growing crystals with the minimum possible defects, the clean and adatom covered surfaces of silicon have been thoroughly investigated. Recent studies on the growth of silicon surfaces have shown that atoms like As, Sb, Te are good surfactants preventing island formation and hence aiding the layer by layer growth. [1–6] In addition, the goal of combining large infra-red detector arrays with relatively thin films of HgCdTe. [7] The atomic configuration of adsorbed layer on the bare Si(001)-(1×1) surface is covered by Te atoms. We also examine the possibility of two adjacent adsorbed Te atoms forming a dimer bond to give a (2×1) reconstruction. Other possible higher order reconstruction geometries are searched for by finite temperature ab-initio molecular dynamics (MD) calculations. We investigate the energetic and reconstruction starting from very low coverage (θ = 0.0625) up to a monolayer coverage (θ = 1). We first determine the binding energies of a single Te atom adsorbed at the special sites of the unit cell for θ < 1. We describe how the original Si–Si dimer bonds of the Si(001)-(2×1) surface are broken, and how eventually the surface is covered by Te atoms. We also examine the possibility of two adjacent adsorbed Te atoms forming a dimer bond to give a (2×1) reconstruction. Other possible higher order reconstruction geometries are searched for by finite temperature, ab initio molecular dynamics method. We find that uncorrelated lateral excursions of bridged Te atoms in flat potential wells hinder the observation of any definitive surface reconstruction pattern at finite temperatures.

Calculations were carried out within the density functional approach using the Vienna Ab-initio Simulation Package (VASP). [13] The wave functions are expressed by plane waves with the cutoff energy |k + G|^2 ≤ 250 eV. The Brillouin zone (BZ) integration is performed by using the Monkhorst-Pack scheme with (2×2×1), (2×8×1) and (4×8×1) special points for (4×4), (4×1) and (2×1) cells, respectively. The convergence with respect to the energy cutoff and number of k-points was tested. Ionic potentials are represented by ultra-soft Vanderbilt type pseudopotentials and results are obtained within generalized gradient approximation for a fully relaxed atomic structure. The preconditioned conjugate gradient method is used for wave function optimization and the conjugate gradient method for ionic relaxation at T = 0 K. At finite temperatures, the Nosé-Hoover thermostat is employed for constant temperature dynamics of atomic motions in the self-consistent field of electrons.
The time step in MD calculations, $\Delta t$, is chosen such that typical phonon time period is divided into a few tens of time steps. We picked $\Delta t$ to be 2 $fs$ to ensure that the ionic trajectories are smooth.

The Si(001) surface is represented by a repeating slab geometry. Each slab contains 5 Si(001) atomic planes and hydrogen atoms passing the Si atoms at the bottom of the slab. Consecutive slabs are separated by a vacuum space of 9 Å. For calculations at $T = 0$ K, Si atoms in the top four atomic layers are allowed to relax, while the bottom Si atoms and passing hydrogen are fixed to simulate bulk-like termination.

In finite temperature calculations, all atoms, including Si and H atoms in the bottom layer, are allowed to move to avoid large temperature gradient. Lattice parameters are expanded according to the temperature under study using the experimental thermal expansion coefficient in order to prevent the lattice from experiencing internal thermal strain. We reproduced the energetics and geometry of the $c(4 \times 2)$, $p(2 \times 2)$ and $p(2 \times 1)$ reconstructions of a clean Si(001) surface using the above parameters. \[1 \]

The binding energy of a single Te adsorbed on the special (on-top T, cave C, hollow H, and bridge B) sites on the clean Si(001) surface are calculated using a supercell consisting of eight ($2 \times 1$) cells. The large size of the supercell ensures that the interaction between the adsorbed Te atoms is negligible so that results can represent low Te coverage. In Fig. 1a, only one ($2 \times 1$) cell of the supercell is shown. The binding energies are found to be T: 4.5 eV, C: 3.5 eV, H: 3.4 eV, and B: 3.2 eV. These binding energies were calculated for fully relaxed structures at $T=0$ K. Apparently, the most energetic site at low coverage is the on-top site, where a Te atom above the dimer bond of the clean Si(001)-($2 \times 1$) surface is bonded to two Si atoms of the same dimer bond. This is consistent with our intuitive chemical notion that Te($5p^3$) tries to fill its outermost p-shell by coordinating with two surface Si atoms. Our result is also in agreement with STM images. \[3 \]

By considering only two special sites, Takeuchi \[13 \] found the on-top site to be energetically more favorable than the bridge sites by 0.8 eV. We examined the stability of the Te atom adsorbed at the on-top site for higher coverages. For $\Theta =0.5$, Te atoms adsorbed 2.25 Å above each surface dimer bond were found stable, except that the underlying Si-Si dimer bond is elongated marginally and the dimer asymmetry is removed. The Si-Te bond length is 2.53 Å which is close to the sum of the Si and Te covalent radii and in excellent agreement with experiment. \[20 \]

A monolayer coverage of Te (i.e. $\Theta =1$) is the most critical insofar as the controversy regarding the surface reconstruction is concerned. We attempt to resolve the controversy by addressing the following issues which are not settled yet. These are: i) How does the configuration of the surface change with increasing $\Theta >0.5$? ii) Can two adjacent Te atoms on the surface dimerize at $\Theta =1$? iii) What is the geometry of the surface recon-
ysis at T=0 K, we performed a finite temperature, ab-initio molecular dynamics calculations at T=600 K and T=1000 K using (4×1) supercell geometry. Figure 2 illustrates the displacements of Te atoms in a (4×1) supercell at T=600 K. The time variation of the mean squared planar displacements, \( \langle u_x^2 \rangle = \frac{1}{3} \sum_{i=1}^{4} (u_{x,i}^2 + u_{y,i}^2) \), (\( u \)'s are the displacements of the atoms from their ideal lattice positions) shows that the system is sufficiently thermalized within \( \sim 1 \) ps. We note that the displacements along the \( z \)-direction, \( u_{z,i}(t) \), are small since the bridged Si–Te–Si bonds are robust. The average of the perpendicular positions of Te atoms on the surface, \( \langle z \rangle = \frac{1}{4} \sum_{i=1}^{4} z_i(t) \), and also those of 8 hydrogen atoms at the bottom drifts along the \( z \)-direction with the same negative velocity, \( d\langle z \rangle/dt \sim -0.7 \text{ Å/ps} \). In addition to this spurious translation of the unit cell, the displacement of each Te atom, \( u_{z,i}(t) \), oscillates with decreasing amplitude and without any correlation with the other Te atoms.

The displacement along the \([110]\) (or \( y \)-) direction, \( u_{y,i}(t) \), is large and can be relevant for a particular reconstruction structure. After the thermalization of the system, \( u_{y,i}(t) \) becomes oscillatory and quasi periodic with periods of the order of \( \sim 1.0 \) ps. The behavior illustrated in Fig. 2 is reminiscent of the surface longitudinal acoustic mode due to Te rows. The amplitudes of oscillations vary between 0.4 Å to 0.7 Å resulting in lateral excursions (as large as 1.4 Å) of Te rows along \([110]\) direction. To enhance the statistics, we performed the same calculation at T=1000 K. The adsorbed Te atoms execute similar motions, only with larger amplitudes, at this higher temperature.

These excursions or displacements of adjacent rows do not display any correlation. Moreover, they are time dependent. The random and uncorrelated nature of the displacements prevents us from deducing a well-defined reconstruction pattern. Such excursions of Te rows along the \([110]\) direction would not give rise to any resolvable pattern in the LEED and STM images. For example, since the period of oscillations are much shorter than the characteristic scan time of STM, the STM images taken at finite temperature would indicate disordered (1×1) reconstruction.

For adsorbed Te rows to execute large amplitude excursions with low frequency at T=600 K is unusual and suggests rather soft and non-Hookian (nonlinear) force constants in this direction. In fact, as seen in Fig. 3, the total energy remains practically unchanged for a displacement of the Te rows of \( u_y \sim \pm 0.5 \) Å. For the displacement of adjacent rows in opposite directions, \( E_T(u_y) \) resembles a double well potential with a broad maximum at \( u_y = 0 \) and a shallow minimum on either sides. The barrier between these two minima is very low, almost at the accuracy limit of the present calculations (7 meV). This suggests that adjacent Te rows are displaced by \( \sim 0.25 \) Å in opposite directions, forming a zigzag chain of Te atoms on the \([110]\) direction and leading to a (2×1) surface reconstruction at T=0 K. Interestingly, except for the disappearance of the weak double well form, the variation of the total energy with \( u_y \) remains essentially unaltered if the adjacent Te rows are displaced in the same direction. This implies that, at finite temperatures, Te rows can easily traverse the weak barrier and execute random (uncorrelated) displacements. This situation is consistent with the results of finite temperature MD calculations summarized in Fig. 2. Since the potential energy well is so flat, the positions of Te atoms would be easily modified by the tip-sample interaction in STM experiments. The total energy curve in Fig. 3, is a fit to an analytical form \( E_T(u_y) = \alpha u_y^2 + \beta u_y^4 + \gamma u_y^6 \) (with \( \alpha = 0.3024 \text{ eV/Å}^2, \beta = 0.6242 \text{ eV/Å}^4, \gamma = -0.2087 \text{ eV/Å}^6 \)) and reflects strong anharmonicity (nonlinearity in force constants) of the potential wells wherein Te atoms move.

In summary, we have found that Te atoms adsorb above the Si-Si dimer bonds at low coverage. There is no energy benefit for forming Te dimers at any coverage. At monolayer coverage, the potential wells for Te atoms are rather flat and strongly anharmonic along the \([110]\) direction. There is almost no barrier for the Te rows on the surface to make significant excursions relative to their ideal positions along the \([110]\) direction. First principle finite temperature calculations indicate that the displacements of Te rows are uncorrelated, lacking any definitive reconstruction pattern.

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As compared to the C, and H site adsorptions, the B site adsorption is not energetically most favorable. However, the energetics change upon coadsorption with the T site.

According to Pauling’s scale, Te is more electronegative than Si (i.e. $\chi_{Te} = 2.0$ and $\chi_{Si} = 1.8$). Therefore, one expects that charge is transferred from Si to Te. This is consistent with the atomic configurations and occupancies, $\text{Te}(5s^25p^4)$ and $\text{Si}(3s^23p^2)$.

Recently, it has been shown that strong anharmonicity of the potential energy is the cause of high temperature superconductivity in MgB$_2$ crystals. T. Yildirim et al. Phys. Rev. Lett. (in press).

FIG. 1. (a) The unit cell of the Si(001)-(2×1) surface. The possible sites for the adsorption of Te at very low $\Theta$ are marked by X. (b) The (1×1) structure of the Te covered Si(001) surface. (c) Charge density contour plots of the Si-Te-Si bonds with arrows showing the direction of increasing charge density. (d) Charge density contour plots on the (001) plane passing through the Te atoms. Large filled, large empty, small empty, and smallest empty circles denote Te, first layer Si, second layer Si, and third layer Si atoms, respectively. The thick lines between circles indicate bonds. x-, y-, and z-axis are parallel to the [1 1 0], [1 1 0], and [0 0 1] directions, respectively. The lattice constant $a = 3.84$ Å.

FIG. 2. Time variation of the displacements of the Te atoms ($u_x$, $u_y$, and $u_z$) from their ideal lattice positions in a (4×1) supercell calculated at T=600 K. The left panel shows the supercell. At t=0, all the atoms are at their ideal lattice positions.
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