Te covered Si(001): A variable surface reconstruction

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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, clean and adatom covered surfaces of silicon have been thoroughly investigated. Recent studies on the growth of silicon and GaAs surfaces have shown that atoms like As, Sb, and Te are good surfactants, preventing island formation and hence aiding layer-by-layer growth.[1–6] In addition, the goal of combining large infrared detector arrays with relatively cheap and well-developed Si integrated circuit technology has led to the growth of HgCdTe on a Si(001) surface. Because of a large ($\sim$19%) lattice mismatch, thick buffer layers of CdTe must be grown before growing active layers of HgCdTe.[7] The atomic configuration of adsorbed Te, which forms the first layer grown on the bare Si(001) surface, is crucial for the fabrication of high-performance devices, since it determines how growth nucleates and hence the quality of the epilayer.[8]

The adsorption of Te on Si(001) surfaces for different coverages and the resulting atomic geometries have been studied by different surface techniques. While the energetically favorable adsorption sites are well understood at low Te coverage,[7,9] the models of surface reconstructions proposed for near monolayer coverage ($\Theta\sim1$) have been at variance.[7,9–13] Most of the low-energy electron diffraction (LEED) experiments observe a (1×1) structure up to temperatures high enough to desorb Te from the surface.[7,9–11] Other experiments report different structures. For example, Tamiya *et al.*[12] found the transition from the low temperature (1×1) structure to a (2×1) structure at $T=873$ K. Wiame *et al.*[13] observed a (2×1) symmetry in their scanning tunneling microscopy (STM) images and proposed an atomistic model involving Te-Te dimers. The differing of the reconstruction geometries from one experiment to another is a puzzling and an uncommon situation.

In this work, we explain this puzzling situation using the results of finite temperature *ab initio* molecular dynamics (MD) calculations. We investigate the energetics of Te adsorption starting from very low coverage ($\Theta=0.0625$) up to a monolayer coverage ($\Theta=1$). We first determine the binding energies of a single Te atom adsorbed at the special sites of the unit cell for $\Theta\ll1$. 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 by a finite temperature *ab initio* MD 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).[14] The wave functions are expressed by plane waves with cutoff energy $|\mathbf{k}+\mathbf{G}|^2\leqslant250$ eV. Brillouin zone (BZ) integration is performed by using the Monkhorst-Pack scheme[16] with $(2\times2\times1)$, $(2\times8\times1)$, and $(4\times8\times1)$ special points for (4×4), (4×1), and (2×1) cells, respectively. The convergence with respect to the energy cutoff and number of $\mathbf{k}$ points was tested. Ionic potentials are represented by ultrasoft Vanderbilt-type pseudopotentials[17] and results are obtained within generalized gradient approximation[18] 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[19] is employed for constant temperature dynamics of ionic motions in the self-consistent field of electrons.[14] The time step in MD calculations, Δt, is chosen such that typical phonon time period is divided into a few tens of time steps. We picked Δt 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 five Si(001) atomic planes and hydrogen atoms passivating the Si atoms at the bottom of the slab. Consecutive slabs are separated by a vacuum space of 9

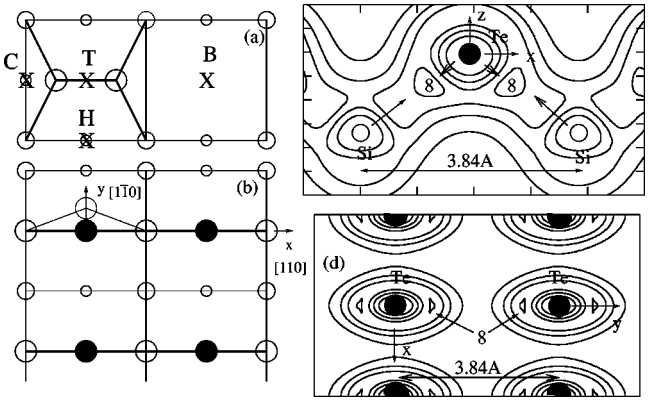

FIG. 1. (a) The unit cell of the Si(001)-(2×1) surface. The possible sites for the adsorption of Te at very low Θ are marked by **X**. (b) The (1×1) structure of the Te covered Si(001) surface. (c) Charge density contour plots of the Si-Te-Si bonds with arrows showing the direction of increasing charge density. (d) Charge density contour plots on the (001) plane passing through the Te atoms. Large solid, large open, small open, and smallest open 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* axes are parallel to the [110], [1$\bar{1}$0], and [001] directions, respectively. The lattice constant $a=3.84$ Å.

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 passivating hydrogens are fixed to simulate bulklike termination.

In finite temperature calculations, all atoms, including Si and H atoms in the bottom layer, are allowed to move to avoid a 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 $c(4\times2)$, $p(2\times2)$, and $p(2\times1)$ reconstructions of a clean Si(001) surface using the above parameters.[15]

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 (2×1) 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. 1(a), only one (2×1) 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)-(2×1) surface is bonded to two Si atoms of the same dimer bond. This is consistent with our intuitive chemical notion that Te($5p^4$) tries to fill its outermost *p* shell by coordinating with two surface Si atoms. Our result is also in agreement with STM images.[9] By considering only two special sites, Takeuchi[20] 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 to be 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.[11]

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: (i) How does the atomic configuration of the surface change with increasing $\Theta>0.5$? (ii) Can two adjacent Te atoms on the surface dimerize at $\Theta\sim1$? (iii) What is the geometry of the surface reconstruction and how does the surface structure vary with temperature at $\Theta\sim1$? To address the first question, we begin with an initial configuration where one Te is adsorbed at the **T** site and the second one at the **B** site on the Si(001)-(2×1) surface, and let this structure relax at $T=0$ K. The occupation of the **B** site at high Te coverage is consistent with experiments.[7,21] In reaching the stable structure, the Te atoms form directional bonds with surface Si atoms while Si-Si dimer bonds elongate and eventually break. It appears that each Si-Si dimer bond is broken to form four new Si-Te bonds. In the final stable structure, Si atoms of the broken dimer bond are pushed to their bulk positions, reforming the outermost, bulklike Si(001) atomic plane. Each adsorbed Te atom is connected to the substrate with two Te-Si bonds of length 2.53 Å. At the end, a metallic Te(001) atomic plane forms 1.65 Å above the Si substrate with a binding energy of 4.28 eV per Te atom relative to the clean Si(001)-(2×1) surface and free Te atom. Figure 1(b) describes the atomic positions of this ideal (1×1) structure of the Te monolayer (ML) on the Si surface. The charge density contour plots in Fig. 1(c) indicate that the bond is directional. The maximum of the charge occurs between Si and Te, but closer to Te.[22] In spite of the directional Te-Si bonds, the surface of Te covered Si(001) surface is metallic with a small density of states at the Fermi level. From force calculations we find that the Te atoms are robust against displacements along the [110] (or *x*) direction in the plane of Si-Te-Si bonds.

Our calculations for a free Te_2 molecule predict a binding energy of 4.41 eV and a bond length of 2.56 Å. This suggests the possibility that two adjacent Te atoms on the Si(001) surface may experience an energy benefit by forming a Te-Te dimer bond by moving towards each other in the *y* direction [see Fig. 1(b)]. Displacement of one of the Te atoms is shown by an arrow. Such a dimerization can once again lead to a (2×1) reconstruction. As a matter of fact, a similar adatom dimerization is known to occur on As covered Si(001) and Ge(001) surfaces and Al covered Si(001) surface.[2,23,24] To test whether Te-Te dimerization can occur and to answer point (ii), an initial structure with a Te-Te distance of 3 Å [which is greater than the bond length of Te_2, but smaller than the undimerized distance in the (1×1) structure] is relaxed at $T=0$ K. Upon relaxation, Te atoms moved away from each other so that the tilted Si-Te-Si plane became perpendicular to the surface and the total energy of the system is lowered significantly. The analysis of the charge density in a (001) (or *xy*) plane passing through the Te atoms suggests

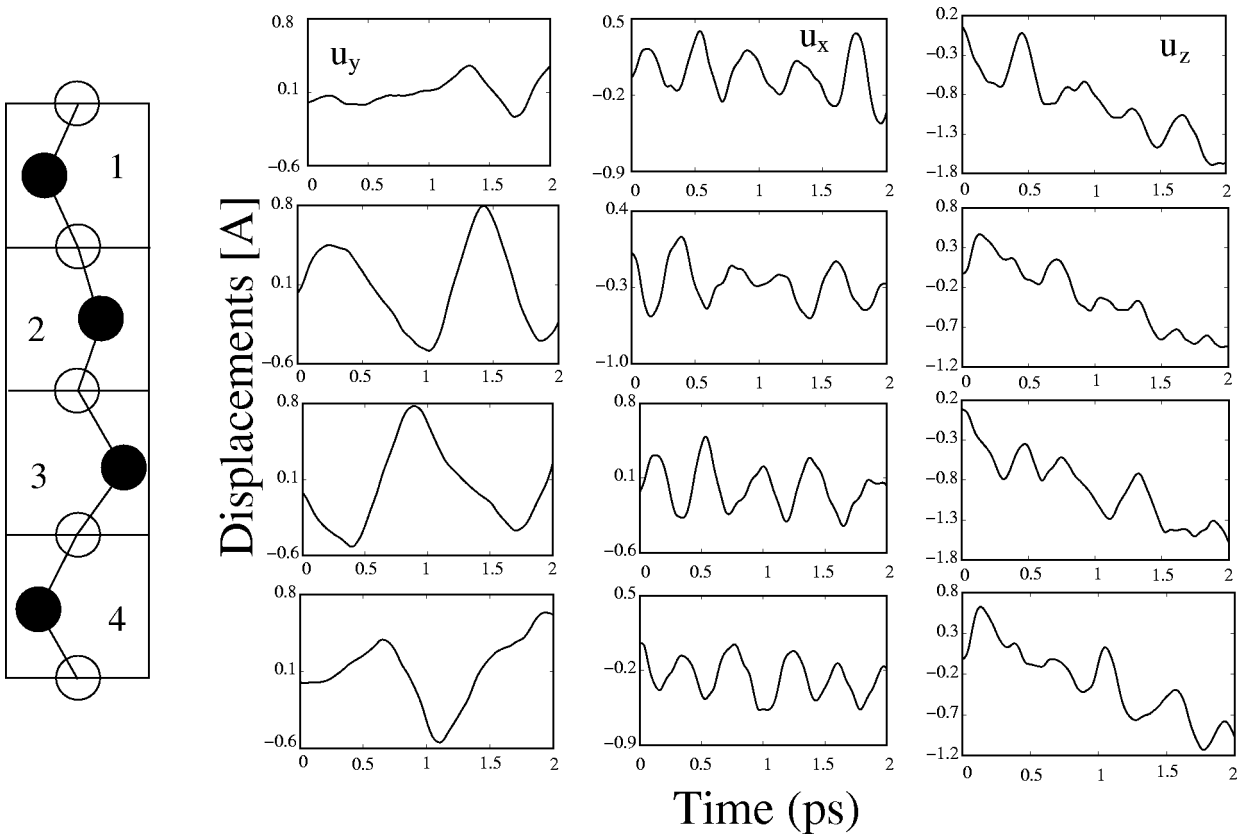

FIG. 2. Time variation of the displacements of the four Te atoms (u_x, u_y, and u_z) from their ideal lattice positions in a (4×1) supercell calculated at $T=600$ K. The left-most panel shows the supercell with the horizontal axis parallel to the [110] (or y) direction. At $t=0$, all the atoms are at their ideal lattice positions.

that the formation of strong Te-Si bonds excludes the bonding between two adjacent Te atoms [Fig. 1(d)]. Simple valence arguments also suggests that Te, being divalent, would tend to avoid bonding with three other atoms.

To address the most significant question (iii) posed above, one must consider the reconstruction at $\Theta=1$ which may involve complex and concerted rearrangements of the substrate and adsorbate atoms at high temperature. To access all possible reconstruction geometries that cannot be easily determined by transition state analysis at $T=0$ K, we performed finite temperature *ab initio* MD calculations at $T=600$ and 1000 K using a (4×1) supercell geometry.[25] 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, $\langle u_{\parallel}^2\rangle=\frac{1}{4}\Sigma_{i=1}^{4}(u_{x,i}^2+u_{y,i}^2)$ (u's are the displacements of the atoms from their ideal lattice positions), shows that the system is sufficiently thermalized within ~1 ps. We note that the displacements along the x direction, $u_{x,i=1,4}(t)$, are small since the bridged Si-Te-Si bonds are robust. The average of the perpendicular positions of Te atoms on the surface, $\langle z\rangle=\frac{1}{4}\Sigma_{i=1}^{4}z_i(t)$, and also those of eight hydrogen atoms at the bottom drifts along the z direction with the same negative velocity, $d\langle z\rangle/dt\sim -0.7$ 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 $[\bar{1}10]$ (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 quasiperiodic with periods of the order of ~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 and 0.7 Å, resulting in lateral excursions (as large as 1.4 Å) of Te rows along the [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 is much shorter than the characteristic scan time of STM, the STM images taken at finite temperature would indicate disordered (1×1) reconstruction. In fact, as mentioned earlier, most of the experiments do indeed report a (1×1) structure at ~1 ML Te coverage. But two experiments have reported a (2×1) reconstruction at high temperatures. This might have been due to experimental conditions, like the tip-sample interaction in STM or the condition of a bare

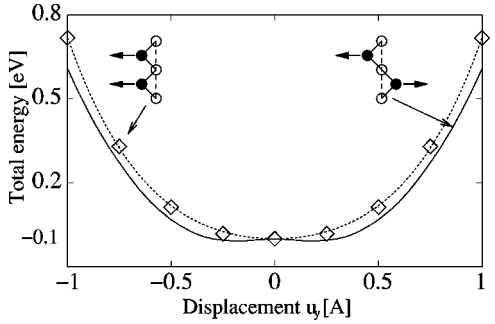

FIG. 3. Variation of total energy with the displacements of the Te row, u_y, calculated at $T=0$ K. Each data point corresponds to a fully relaxed structure under a given displacement of the Te rows along the [110] (y) direction. The solid line is for the adjacent rows moving in opposite directions forming a zigzag pattern. ◇'s correspond to the Te rows moving in the same direction. An analytical fit $E_T(u_y)$ to the total energy values depicted by the ◇'s is shown by the dashed line. Energies are measured with respect to the perfect (1×1) surface for $u_y=0$.

Si(001) surface. We hope a future experiment will resolve this controversy decisively.

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 $u_y\sim\pm0.5$ 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 ~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 $\alpha=0.3024$ eV/Å^2, $\beta=0.6242$ eV/Å^4, $\gamma=-0.2087$ eV/Å^6) and reflects the strong anharmonicity (nonlinearity in force constants) of the potential wells wherein Te atoms move. Such strong anharmonicity has been shown to cause dynamical alternation between $c(4\times2)$ and $p(2\times2)$ reconstructions of a clean Si(001) surface at finite temperatures.[26,27]

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-principles finite temperature calculations indicate that the displacements of Te rows are uncorrelated, lacking any definitive reconstruction pattern.

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