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Atomic structure of the Te/Si(100)-(2×1) surface

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We investigated the atomic structure of the Te/Si(100)-(2×1) surface using the density functional theory. A new model of reconstruction for this surface, based on a two-layers scheme, is proposed. In this model, Te atoms are situated in twofold bridge sites in the first two layers. Small shifts of Te atoms, with respect to the perfect bridge positions, are noticed in one of the two layers and probably give rise to a slightly disordered surface. This model is in agreement with all the experimental data available and in particular with the experimentally observed Te coverage of one monolayer. Comparison between total energies obtained for this surface and the Te/Si(100)-(1×1) surface shows a better stability for the (2×1) in agreement with what has been reported in the literature.

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I. INTRODUCTION

The chemisorption of group-VI elements such as S, Se, or Te on Si has been the subject of numerous studies,[1] motivated by fundamental issues (concerning, for example, the understanding of the reconstruction of semiconductor surfaces) as well as more technological reasons, related to passivation, heteroepitaxy and growth. The adsorption processes on the Si(100) surface, which is widely used in the microelectronics industry, were particularly investigated.

From the fundamental point of view, the mechanisms that govern the reconstruction of the elemental semiconductors are not yet fully understood. Indeed, even if the tendency of the system to saturate the dangling bonds arising from the existence of the surface is well known and is often seen as the driving force of the reconstruction process, other aspects like stress are to be considered. Adsorption of group-VI elements on Si(100) is expected to result in a complete dereconstruction of the surface: Each of the adsorbate atoms bonding to two Si atoms and presenting two filled orbitals outwards the surface, restoring the ideal (1×1) periodicity. Although results obtained for the adsorption of Se and S are not completely conclusive, in the case of Te on Si(100), a (1×1) symmetry has been observed in certain conditions.[2,3]

More specifically, the Te/Si interface is used for the growth of high quality layers of CdTe on Si(100), which enter in the fabrication of $Hg_xCd_{1-x}Te$-based infrared detector arrays.[4,5] In addition, Te acts as a surfactant in the growth of Ge on Si substrate.[6–8]

Despite their technological importance, the structures of the Te layers adsorbed on Si(100) substrates are still the subject of debate. While the (1×1) structure seems to be almost fully understood,[3,9,10] (2×1) and (3×1) reconstructions were observed[11–13] which are until now almost unexplained. Sen *et al.*[14] claimed recently that one reason could be that tellurium covered Si(100) would not have a well-defined structure due to soft longitudinal modes of surface phonons preventing the reconstructed structure from attaining any permanent periodic geometry. While it has been shown by Takeuchi[10] that indeed the (1×1) structure is not perfectly ordered, one should remark that the computations by Sen *et al.*, carried out at 600 and 1000 K, can not be compared to observations performed at room temperature after annealing at such temperatures.

The main difference between these various structures is the preparation procedure.[15] Several methods have been reported in the literature: The deposition of tellurium on a Si(100)-(2×1) surface both at room temperature[16] and at 400 K[7] leads to the same structure with (1×1) symmetry. This (1×1) structure is also obtained by room temperature adsorption of a thick layer of Te[2] or CdTe[3,17] followed by annealing at around 600 K. Direct deposition of CdTe on samples at elevated temperature also leads to the same surface structure.[17] In the latter growth method the Cd desorbs from the surface leaving one monolayer (ML) of Te. The other structures of Te/Si(100), studied by low energy electron diffraction[11,12] (LEED) and scanning tunneling microscopy (STM),[11] are (2×1) and (3×1) reconstructions which are obtained by annealing the (1×1) surface, prepared by Te deposition at room temperature, to 900 and 950 K, respectively.

The purpose of this paper is to propose a new reconstruction model of the Te/Si(100)-(2×1) surface taking into account the stability of this structure and to compare this stability with the (1×1) structure.

II. METHOD OF CALCULATION

Calculations were performed in the framework of the density functional theory (DFT),[18,19] within the local density approximation using norm-conserving pseudopotentials.[20] A

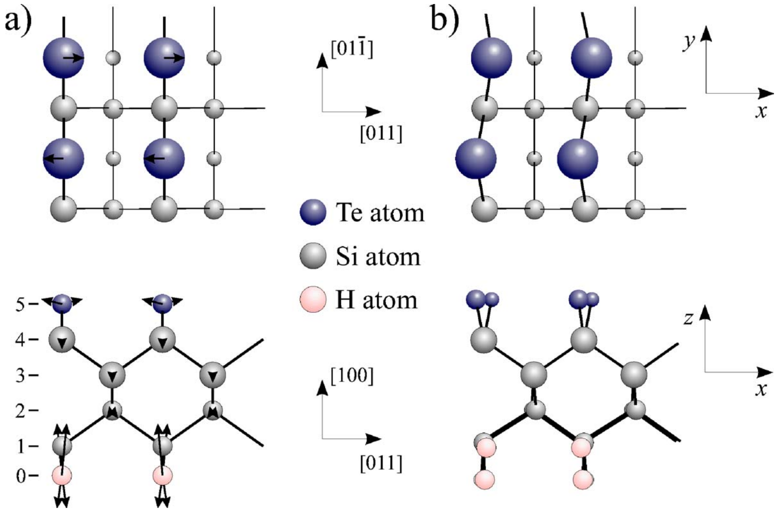

FIG. 1. (Color online) (a) Unit cell used for the simulation of the Te/Si(100)-(1×1) surface. (b) Final configuration after relaxation. The arrows indicate the movements of the atoms after relaxation of the atomic position; their length is proportional to the amplitude of the displacement. The size of the atoms depends on the distance to the observer.

combined electronic and ionic conjugated gradient algorithm[21,22] was used to obtain the optimal surface structures. The wave functions were expanded in a plane wave basis set with a cut-off energy of 30 Ha. Brillouin zone integration was performed using four **k**-points (Monkhorst-Pack scheme)[23] for the (2×2) unit cell (see below) and 16 for the (1×1). The convergence with respect to the cut-off energy and to the number of **k**-points was checked.

To simulate the Si(100) substrate, we used a repeated slab geometry with each slab (Figs. 1 and 2) consisting of 4 layers of Si atoms (labeled 1–4). The convergence with respect to the number of layers of Si was checked on the full model [shown in Fig. 2(a)]: Going from 4 to 5 layers of Si changed atomic positions by less than 0.01 Å. The back-side Si was saturated by H atoms in dihydride configurations (layer 0) in order to prevent its reconstruction. The surface unit cell was (2×2), allowing us to consider (2×1) reconstructions. Te atoms (layer 5) were initially placed at the bulk silicon position.

The first configuration studied (not shown) is a reference (1×1) unit cell with only one Te atom. Next, Fig. 1(a) shows a configuration where the (1×1) symmetry may be broken by the relative displacement of Te atoms. For the configuration corresponding to the Te/Si(100)-(2×1) structure [Fig. 2(a)], layer 5 was composed of Te and Si in equal proportion and layer 6 of 1/2 ML of Te.

The total amount of Te at the surface corresponds to 1 ML for both structures. The empty space between two slabs is converged at approximately 12 Å.

III. RESULTS AND DISCUSSION

A. Te/Si(100)-(1×1)

In recent years, the structure of the Te/Si(100)-(1×1) surface has been the object of several investigations, both experimental[2,3] and theoretical[9,10,14] which agreed to conclude that the surface consists in a 1 ML Te-terminated surface on which the Te atoms are saturating the Si dangling bonds in twofold bridge sites above the fourth layer Si atoms.

Our computations performed on the reference (1×1) unit cell tend to confirm this structure. The distance between Te and Si atomic planes, $\Delta z_{\text{Te–Si}}=1.56$ Å and Te–Si bond

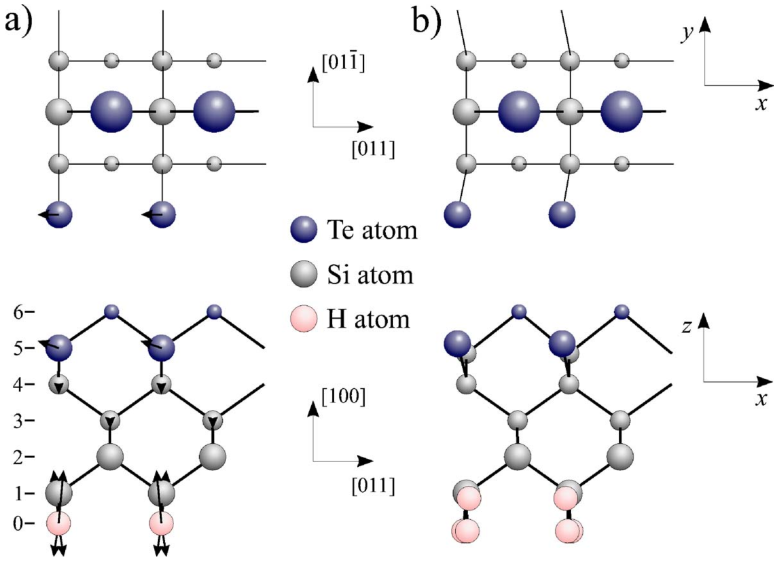

FIG. 2. (Color online) (a) Unit cell used for the simulation of the Te/Si(100)-(2×1) surface. (b) Final configuration after relaxation. The arrows indicate the movements of the atoms after relaxation of the atomic positions; their length is proportional to the amplitude of the displacement. The size of the atoms depends on the distance to the observer.

length, $d_{\mathrm{Te-Si}}$ is equal to 2.47 Å. The distance between Si layers 3 and 4, Δz_{34} is almost unchanged to 1.32 Å (1.35 Å in the Si bulk). The Te atom does not stay in the ideal diamond Si site, and is displaced by 0.24 Å in the plane.

For the (2×2) surface unit cell with a uniform Te ML shown in Fig. 1, two consecutive Te rows are shifting in opposite directions by 0.5 Å with respect to each other, giving rise to a local (2×1) periodicity (the Si sublayers do not move perceptibly). However, calculations by Takeuchi[10] indicate that consecutive rows can shift in the same direction, thus excluding this particular configuration of possible models for the (2×1) structure, and that the energy difference between these two configurations is less than 0.01 eV/(1×1). To confirm this, we compare the computed total energy to the one of the relaxed reference (1×1) unit cell with only one atom of Te. We obtain energies 0.03 eV/(1×1) lower than the (1×1) structure, in good agreement with Takeuchi. This small energy difference between the "relaxed" and the true (1×1) makes unlikely the existence of a stable structure at room temperature. The row shift is probably due to the stress induced by the higher covalent radius of the Te with respect to that of the Si. On real (1×1) surfaces, the existence of missing Te lines in a direction perpendicular to Te rows reduces the surface stress[2,10] by allowing the Te to relax by increasing the distance between Te atoms.

On the back-side of the slab we observed a tilting of the dihydride group with respect to the surface in agreement with literature.[24,25]

The calculated $d_{\mathrm{Te-Si}}$ is equal to 2.48 Å while $\Delta z_{\mathrm{Te-Si}}$ is 1.55 Å. These values are comparable with those found by Miwa *et al.*:[9] 2.53 and 1.65 Å, respectively.

B. Te/Si(100)-(2×1)

In a previous article,[11] we reported on the STM observation of the Te/Si(100)-(2×1) surface. Based on STM images as well as, Auger electron spectroscopy (AES), and x-ray photoemission spectroscopy (XPS) coverage estimations, we suggested a Te-dimer model. At that time, we pointed out several problems with this structure, such as the excess of electrons at the surface, in disagreement with the well-known electron counting model.[26] However, in spite of its weakness, it was the only model which was consistent with all the experimental results found in the literature.

We first tested this model, and came to the conclusion that the formation of Te dimers is energetically unfavorable as also found by Miwa *et al.*[9] These authors propose instead a (2×1) model made of Si-Te mixed dimers for a coverage of 1/2 ML. Besides the fact that the coverage is only half of the 1 ML value measured on the real (2×1) surface, the calculated formation energies indicate that this atomic configuration is not energetically favorable, in disagreement with observations by Ohtani.[12] Indeed, the (2×1) structure is irreversibly obtained after annealing of the (1×1) surface. Moreover, as shown by temperature desorption experiments,[13] no desorption is observed in the phase transition $(1\times1)\rightarrow(2\times1)$, indicating a better stability for the (2×1) structure. To completely remove the last Te layer, a temperature of almost 1050 K is needed.

TABLE I. Comparison of the interlayer distances (in Å) for the different models: The initial configuration Te/Si(100)-(1×1), Te/Si(100)-(1×1) after relaxation (Fig. 1), and our new (2×1) model (Fig. 2). The last line gives the total energy difference [per (1×1) unit cell] between the structures.

	1×1	"relaxed" 1×1	2×1
Δz_{34}(Si–Si)	1.32	1.34	1.34
Δz_{45}(Si–Si)			1.29
Δz_{45}(Te–Si)	1.56	1.57	1.58
Δz_{56}(Te–Si)			1.59
Δz_{56}(Te–Te)			1.30
$\Delta\Omega$ (eV)	0.0	−0.03	−0.13

We therefore propose a new model taking into account these observations. As previous results indicate, the stresses in the Te layer seem to play an important role. The structural model of the (2×1) we propose is deduced from this assumption. In order to reduce the strain in the Te layer, we distributed the Te atoms into two layers at the surface, as shown in Fig. 2. In this configuration, the *p*-orbitals of the upper Te atoms are not interacting with any additional atoms.

The displacements of the layer after relaxation are summarized in Table I. With respect to the second full layer of Si (layer 3), the next layers relax significantly. Reference values for the Δz are taken from the relaxed surface presented in Fig. 2(b). The $\Delta z_{\mathrm{Te-Si}}$ and $d_{\mathrm{Te-Si}}$ observed in both Te layers are identical to those observed on the (1×1) surface, to within 0.02 Å. However, the 1/2 ML of Si is compressed as the top Te half-layer descends. The Te sub-layer (layer 5) is also shifted with respect to the Si lattice, by 0.4 Å along the row of Te atoms. In this two-layers model, only the Te atoms in the layer 5 are interacting with the neighboring Te atoms, while the Te atoms of the layer 6 are completely relaxed and show no shift.

This structural model is consistent with our STM images previously published[11] in which alternating bright and dark rows composed of dots separated by the surface lattice parameter show a (2×1) symmetry.

C. Comparison of the (1×1) and (2×1) structures

The first thing to note when comparing the two structures, is that the unit cells used do not contain the same numbers of atoms. As the number of Te atoms per (1×1) unit cell is the same, the comparison does not depend on their chemical potential. By contrast, two additional Si atoms are present in our (2×1) model structure (Fig. 2), compared to the simple monolayer (1×1) structure (Fig. 1). The chemical potential for Si, however, is fixed by that of the substrate, that we compute independently. The difference between the formation energies of both configurations can thus be expressed as

$$\Delta\Omega = E[\mathrm{Te/Si(100)\text{-}(2\times1)}] - E[\mathrm{Te/Si(100)\text{-}(1\times1)}] - n_{\mathrm{Si}}\mu_{\mathrm{Si}} \qquad (3.1)$$

where E is the total energy associated with one configuration and μ_{Si} the chemical potential of a Si atom, and n_{Si} the number of excess Si atoms (1 per Te pair in our new model). The new model is $-0.10\ \mathrm{eV}/(1\times1)$ lower in energy with respect to the relaxed Te monolayer (1×1) structure. This could be explained by the fact that only half of the Te atoms at the surface are interacting with more neighbors, probably reducing the surface energy. It seems that the stress in the Te layer plays a crucial role in the reconstruction of the surface. Indeed, the existence of missing Te lines on the so-called (1×1) surface has been shown and the effects of relaxation have been theoretically demonstrated. We did not observe this kind of feature in our own STM images, probably indicating a relief of the surface stress due to the reconstruction of the surface. One should remark that the preparation method may influence the final quality of the (2×1) surface. Indeed, it has been observed that the Te coverage on the (1×1) saturates at approximately 0.8 ML due to the missing Te lines. The deposition of Te above the phase transition temperature (900 K) gives a (2×1) surface with full monolayer coverage.

IV. CONCLUSIONS

We propose a new structural model for the Te/Si(100)-(2×1) interface resulting from our experimental investigations and from the highlighting of the importance of the stress on the structure of the simpler and better known (1×1) surface. The direct comparison of the computed total energies of the (1×1) structure with our model indicates a stronger stability of the reconstructed surface. This result is in agreement with the experimental fact that the (1×1) structure is irreversibly converted into (2×1) after annealing at 900 K. Moreover, to our knowledge, our model is the only one which is consistent with all the experimental results available to date.

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