Theoretical Study of Si(001)/Te - (1×1), (2×1) and (3×1) Surfaces

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Received February, 1998

The atomic geometry, chemical bonding and energetics for full -, 2/3, 1/2 and 1/3 of a monolayer of Te coverages on the Si(001)/Te - (1×1), (2×1), and (3×1) surfaces have been studied employing first - principles total-energy calculations. For one monolayer coverage we find that the (1×1) structure is energetically favourable against (2×1) structure, in agreement with experimental results, indicating that the dimerization of Te atoms is not an exothermic process. For a coverage of 2/3 of a monolayer, the formation of Te-Si-Te mixed trimers, in a (3×1) - reconstruction, is an energetically stable configuration. At 1/3 coverage, we have obtained the formation of Si-Si dimers with a single Te atom, at the surface in a (3×1) - reconstruction. In this structure there is a very weak interaction between the dimer and the single Te atom.

I Introduction

The morphology and the structural properties of the tellurium-silicon system have been recent subjects has been recently the subject of many experimental works [1-10] However, adsorbed structures of Te on Si(001) surface, Si(001)/Te, are still subject to considerable discussion, with various unresolved claims concerning local geometry, stability, and Te interdiffusion, such as the use of Te as a surfactant in the growth of Ge thin films on Si [5, 6], and the growth of high quality CdTe thin films on Si [7]. Experimental measurements as Low Energy Electron Diffraction (LEED), Surface Extended X-Ray Adsorption Fine Structure (SEXAFS), and Scanning Tunneling Microscopy (STM), indicate that the deposition of full monolayer (ML) of Te atoms at room temperature leads to a (1×1) reconstruction of the surface [1,2,3,8,9].

The aim of this paper is to improve and clarify the understanding of the basic mechanisms that underline the deposition of Te on Si(001). We have performed first-principles pseudopotential density functional calculations on a number of possible configurations of the Te-covered Si(001) surface in the (1×1), (2×1) and (3×1) reconstructions. In particular, we have studied in detail the local atomic geometry, chemical bonding, and energetics of 1/3, 1/2, 2/3 and full-monolayer (ML) coverages. For a full ML coverage our results confirm the experimental observations [1, 2, 3, 8, 9]. For lower coverage, 2/3 ML, our results confirm the experimental observations of Tamiya et al. [10] of a mixed Te-Si-Te trimers in a (3×1) reconstruction.

II Method of Calculation

Our calculations were performed in the framework of the density functional theory [11], within the local density approximation using the Ceperley-Alder correlation [12] as parametrized by Perdew and Zunger [13] . The electron-ion interaction was treated by using norm-conserving, *ab initio* fully separable pseudopotentials [14]. The wave functions were expanded in a plane wave basis set with a kinetic energy cutoff of 8 Ry. The theoretical equilibrium lattice constant of 5.40 Å was used to Si substrate, which is very close to the experimental value (5.43 Å). We adopted the Car-Parrinello approach [15] for electronic structure calculations with a modified computational code due to Stumpf and Scheffler [16].

In order to simulate the Si(001) surface we used the repeated slab method. The slabs contain eight layers of Si, with one side covered by Te atoms. The length of the

vacuum region was assumed to be approximately five monolayers of Si. To avoid the artificial electrostatic field which arises from the periodic boundary condition, we used the planar dipole layer as proposed by Neugebauer and Scheffler [17] and a layer of hydrogen atoms to saturate the botton layer Si dangling bonds. The electronic charge density was calculated by using sets of special $k_{\parallel}$ points in the irreductible part of the surface Brillouin Zone in a following way: we have used four special $k_{\parallel}$ points to (2×2) cell and six special points to (3×1) cell. The equilibrium atomic geometry was obtained by relaxing the top four layers.

III Results and Discussion

Initially we have studied the geometrical configuration of Si(001) - (2 × 1), clean surface, covered by a full ML of Te atoms. Our results indicate that the formation of Te-Te dimers is not an energetically favourable process, and the equilibrium structure is a Si(001)/Te - (1 × 1) reconstructed surface, in agreement with the experimental results [1, 2, 3, 8, 9]. This structure obey the electron counting rule (ECR), although this rule does not work in some situations [18]. Figure 1a shows the respective total charge density of Te atoms, where the non-dimerization of Te atoms is clearly verified. In the equilibrium configuration the bond length between Te(surface) and Si(substrate) is equal to $d_{Te-Si} = 2.53$ Å, and the interplanar distance along [001] direction is $\Delta Z_{Te-Si} = 1.65$Å. These results present a good agreement with experimental measurements of Burges *et al.* [8], $d_{Te-Si} = 2.52 \pm 0.05$ Å and $\Delta Z_{Te-Si} = 1.65 \pm 0.03$ Å. The interplanar distance between Si(first-layer) and Si(second-layer) reduces to 1.33 Å, and all the other interplanar distances underneath are bulk-like (1.35 Å). Therefore, the adsorption of one ML of Te atoms on the Si(001) surface preserve the bulk-like structure of the Si substrate. We have also searched for an energetically stable (or metastable) configuration forming a Te-Te buckled-dimer. Our calculations indicate a monotonical increase of the total energy as a function of the Te atomic displacement, towards each other, until the $d^{dimer}_{Te-Te} = 2.98$ Åthat increases the total energy in 0.82 eV/dimer.

For a coverage of Te atoms equal to 2/3 ML, we have considered a (3 × 1) reconstruction, as proposed by Tamiya *et al.* [10]. Figure 1b shows the total charge density between Te-Si-Te atoms on Si(001), where we can verify the formation of a mixed trimer, Te-Si-Te. In the equilibrium configuration, the mixed trimer presents a bond length of $d^{trimer}_{Te-Si} = 3.08$ Å, which indicates a weak covalent character of these bonds (the sum of the respective covalent radius is equal to 2.49 Å). We have also analised the possibility of formation of Te-Te dimers, occompanied with a single Si atom in a (3 × 1) - reconstructed surface, as recently was proposed by Wiane *et al.*[19]. Again we did not find any stable configuration for Te-Te dimer.

Next we have verified the formation of mixed Si-Te dimers on Si(001)/Te - (2×1) reconstructed surface, for a coverage of 1/2 ML. An energetically stable configuration for this structure is found, and figure 1c exhibit the mixed symmetric Si-Te dimer. In this configuration, with a coverage of half a monolayer of Te, all the surface dangling bonds are completely occupied, obeying the ECR, with a resulting semiconducting band structure.

Finally, for a coverage of 1/3 ML, we have obtained the formation of Si-Si dimer, accompanied by a single Te atom in a (3×1) - reconstruction. In this case the Si dimer bond length is equal to 2.28 Å and the distance between Si(substrate) and Si(dimer) atoms is equal to 2.30 Å. This results are very close to the respective values on Si(001) - (2 × 1) clean surface. The geometrical configuration of the single Te atom is almost equal to the configuration of Si(001)/Te - (1×1) with 1 ML coverage. Therefore, we can infer a weak interaction between Si dimer and single Te monomer, figure 1d. This structure is very similar to that proposed by Wiane *et al*[19], but with the exchange of Te and the Si atoms and a lower Te coverage (1/3 ML).

IV Conclusion

We have performed first-principles total-energy calculations to determine the geometrical structure of Si(001)/Te surface, as a function of Te coverage on Si substrate. Our results indicate that for a full ML of Te coverage, the surface presents a (1 × 1) reconstruction, in agreement with experimental results, and the dimerization of the surface Te atoms is not an energetically favourable configuration. Reducing the Te coverage to 2/3 ML, we have obtained the formation of Te-Si-Te mixed trimers, in a (3×1) reconstruction, as experimentally observed. We did not find any stable configuration of Te dimers for this coverage. For 1/2 ML and 1/3 ML coverages, we have found the formation of (2 × 1) and (3 × 1) reconstructions, respectively. The Si(001)/Te - (2 × 1) presents the formation of mixed Te-Si dimers, where the buckling process of these dimers is not energetically favourable. The Si(001)/Te - (3 × 1), 1/3 ML coverage, presents a Si dimer and a Te monomer, with a very weak interaction between them.

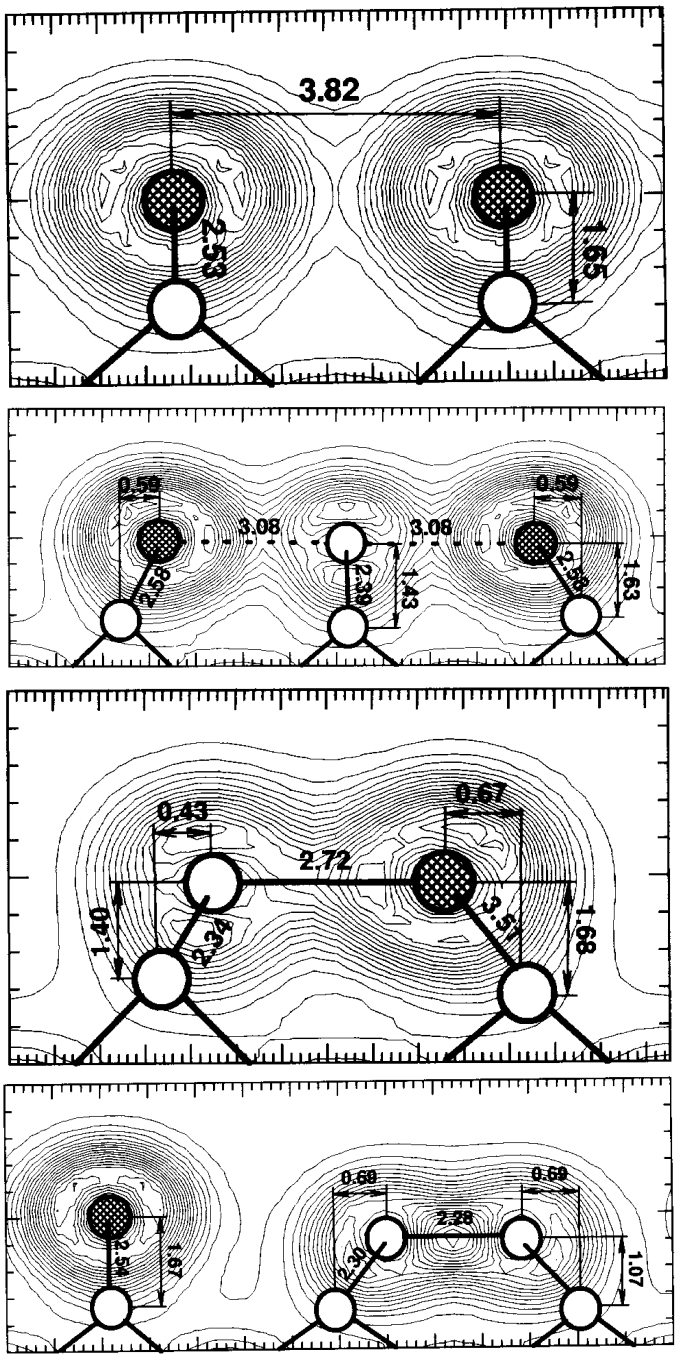

Figure 1. Geometry and total charge density of Si(001):Te surface: (a) (1×1) structure with a full monolayer coverage, (b) (2×1) structure and half-monolayer coverage, (c) (3×1) structure covered by mixed Si-Te dimers (2/3 coverage) and (d) 3 × 1 structure covered by Si-Si dimers (1/3 coverage). The relative distances are in Å.

Acknowledgments

The authors would like to thank the Brazilian agency FAPEMIG for financial support, and CENAPAD MG-CO, and CENAPAD-Unicamp for computational facilities.

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