Theoretical Study of Surfactant Action of Te on Si(001)/Ge Surfaces

R. H. Miwa and E. K. Takahashi

Departamento de Ciências Físicas, Universidade Federal de Uberlândia, C.P. 593,
38400-902, Uberlândia, MG. Brazil

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We have performed first-principles total energy calculations to investigate the adsorption process of Ge on Si(001)/Te, and the surfactant action of Te during the epitaxial deposition of Ge on Si(001)/Te, based on an atomic exchange process, Ge↔Te. The total energy calculation indicates that the adsorption of Ge atom in "vacancy" site is energetically more favourable than its adsorption in "bridge" site. The adsorption of Ge in "on-top" and "anti-bridge" sites can be ruled out. The segregation process of Te atoms, based on an atomic exchange mechanism, reduces the total energy of the surface, confirming the surfactant effect of Te atoms.

I Introduction

The epitaxial deposition of Ge on a Si substrate has attracted many experimental and theoretical studies. However, the growth process of Ge on a Si substrate obeys the Stranski-Krastanov model, giving rise to the formation of Ge 3D islands after deposition of about three monolayers of Ge. Recently, Bennett et al. [1], and Higushi and Nakanishi [2] verified the surfactant effect of Te during epitaxial deposition of Ge on Si(001). The 2D (layer-by-layer) growth regime of Ge on Si was extended to about 200 Å. Bennett [1] proposed an atomic exchange process between the deposited Ge and the surface Te atom, for the segregation process of Te towards the growth surface, reducing the surface total energy of the system.

In the present work we investigate the adsorption process of Ge on Si(001)/Te, and the surfactant action of Te during the epitaxial deposition of Ge on Si(001)/Te.

II Method of Calculation

Our calculations were performed in the framework of the density functional theory (DFT) [8], within the local density approximation (LDA), and using the Ceperley-Alder correlation [9], as parametrized by Perdew and Zunger [10] . The electron-ion interaction was treated by using norm-conserving, *ab initio* fully separable pseudopotentials [11]. 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 for the Si substrate, which is very close to the experimental value (5.43 Å), since we are studying the deposition of Ge atoms on Si(001) surface. We also adopted the Car-Parrinello approach [12] for the electronic structure calculations with a modified computational code due to Stumpf and Scheffler [13].

In order to simulate the Si(001) surface we used the repetead slab method. The slabs contain eight layers of Si, with one side covered by Te atoms. The length of the vaccuum 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 [14] and a layer of hidrogen atoms to saturate the bottom layer Si dangling bonds. The electronic charge density was calculated by using sets of special $k_{\|}$ points in the irreductible part of Brillouin Zone. We have used four special $k_{\|}$ points to 2×2 cell. The equilibrium atomic geometry on the top four layers was obtained by calculating the Hellmann-Feynman forces until magnitudes of 25 meV/Å ($\approx$ 1.8 mRy/Å).

III Results and Discussion

Initially, we have studied the adsorption process of Ge atom on Si(001)/Te - 1×1 surface with coverage of one monolayer of Te atoms, whose occurrence was verified experimentally [3, 4, 5, 6, 7]. We have considered four possible adsorption sites: "bridge", "vacancy", "anti-bridge", and "on-top", as indicated in Fig. 1. The calculated adsorption energy is defined as the total energy difference between Si(001)/Te surface, adsorbed by a single Ge atom, and the clean Si(001)/Te - 1×1 surface, with a Ge atom in a faraway position from the surface. Our results indicate that the adsorption of Ge atom in "vacancy" site is energetically more favourable than the adsorption of Ge in "bridge" site. The adsorption energy difference is equal to 0.20 eV/atom. The Ge adsorption in "on-top", and "anti-bridge" sites are energetically less favourable. A summary of the adsorption energy, and the respective minimum energy Te-Ge bond length are indicated in Table I. Although the adsorption of Ge in the "bridge" site is not the energetically optimum configuration, in this site the bond length between Ge and Te atoms is very close to the sum of the respective covalent radii, 2.59 Å, which indicates a covalent character of the bonds. On the other hand, in the "vacancy" site, the Ge atom is fourfold coordinated, and the Ge-Te bond length is 0.35 Å greather than the sum of the covalent radii.

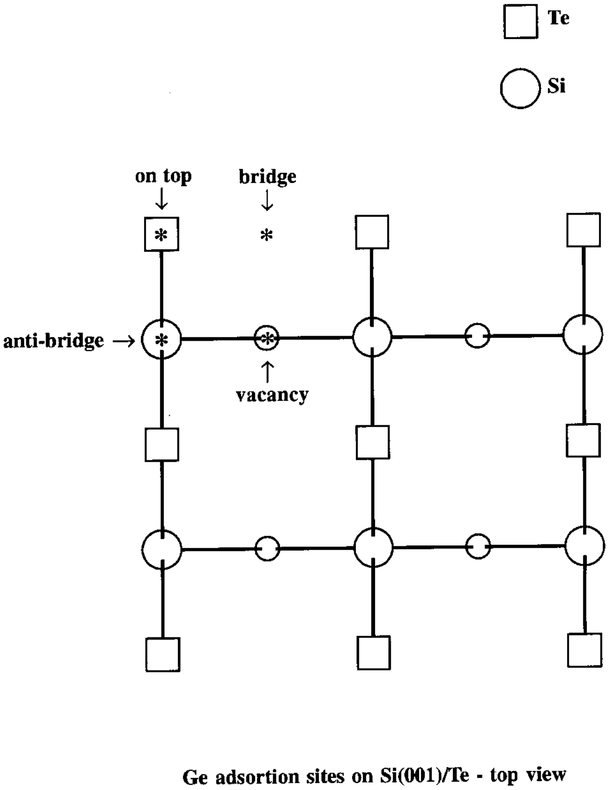

Figure 1. Adsorption sites of Te on Si(001) - 2×1, clean surface, "cave" - C, "bridge" - B, "anti-bridge" - A, and "vacancy" - V.

Table 1. Adsorption energy of Ge atom on Si(001)/Te - 1×1 surface, adsorption energy difference (relatively to "vacancy" site), and the bond length between adsorbed Ge atom and Te.

Site	$E^{Ads.}$ (eV/atom)	$\Delta E^{Ads.}$ (eV/atom)	d_{Te-Ge}
vacancy	-3.65	0.00	2.94
bridge	-3.45	0.20	2.61
on-top	-2.09	1.55	2.40
anti-bridge	-2.66	0.99	2.65

In order to study the surfactant effect of Te atoms, we have considered an atomic exchange process between adsorbed Ge atom in "vacancy" site ("bridge" site), and the substrate Te atom, as proposed in the experimental study of Bennett et al. [1] (see figure 1e). For this atomic exchange process we obtained a reduction of the total energy by 1.12 eV/atom (1.32 eV/atom), indicating an exothermical process, and confirming the surfactant effect of Te, in agreement with the model proposed by Bennett et al. [5]. The exchanged Te atom occupies a surface "bridge" site, twofold coordinated, and the bond length between Te and Ge atom is equal to 2.55 Å, increasing the covalent character of the bond. The exchanged Ge atom occupies the Te site, and the bond length between Ge and sublayer Si atom is equal to 2.37 Å, which also indicates a covalent character of the bond. The sum of the respective covalent radii is equal to 2.39 Å.

During the initial process of the deposition of Ge on Si(001)/Te, there is the possibility of the formation of Ge dimers before Ge↔Te atomic exchange. Therefore, we have studied the energetic and strucutural aspects of the formation of Ge dimers on Si(001)/Te. Our results indicate that the formation of Ge dimers is an exothermical process, where the cohesion energy of the dimers is 0.81 eV/dimer, with a bond length of 2.52 Å. The buckling process of Ge dimers on Si(001) - without a coverage of Te monolayer - has been verified experimentally by Fontes et al. [15], and confirmed theoretically [16, 17]. We have also verified the possibility of the buckling process of Ge dimer on Si(001)/Te. Our results have shown that the buckling of the Ge dimer represents a metastable configuration, with a buckling angle of 16^o and $d_{\mathrm{Ge-Ge}}$ = 2.39 Å. The total energy increases by 0.31 eV/dimer, relatively to the Ge symmetric dimer. Therefore, we can infer that the presence of the Te monolayer on Si(001) avoid the buckling of the Ge dimer. The Te monolayer acts as a buffer layer against the deformation of Si sublayers. To verify the surfactant effect of Te atoms for Ge dimer, we have simulated a dimer exchange process, between Te atoms and Ge dimer. Our results showed that this exchange process reduces the total energy by 0.67 eV/dimer, also confirming the surfactant effect of Te. After Te↔Ge exchange, the surface Te atoms do not dimerize.

Finally we have considered a full monolayer of Ge on Si(001)/Te. In this case, the surface Ge atoms are dimerized, with $d_{\mathrm{Ge-Ge}}$ = 2.51 Å, and the buckling of the dimers is not energetically expected. The bond length between Te(sublayer) and Ge(surface) atoms, is equal to $d_{\mathrm{Ge-Te}}$ = 2.74 Å. The complete exchange between Te and Ge layers is an exothermical process, being the total energy reduced by 0.97 eV/atom, in agreement with the surfactant effect of Te. The surface Te atoms present a 1×1 reconstruction, and the bond length between Te(surface) and Ge(sublayer) atoms was reduced by 0.11 Å, $d_{\mathrm{Te-Ge}}$ = 2.63 Å. The surface Te dangling bonds are dubly occupied, which avoid the formation of the Te dimers, giving rise to 1×1 reconstruction.

IV Conclusion

We have performed a theoretical investigation of adsorption process of Ge on Si(001)/Te surface, and the surfactant action of Te atoms. Our results indicate that the adsorption of Ge atom in "vacancy" site is energetically more favourable than the adsorption in "bridge" site. The adsorption of Ge in "on-top" and "anti-bridge" sites can be ruled out. The surfactant effect of Te atoms was verified based on an atomic exchange process between adsorbed Ge atom and the surface Te atom. Our total energy calculation showed that this atomic exchange is an exothermical process, confirming the surfactant effect of Te atoms. Next, we have considered the formation of Ge dimer on Si(001)/Te. The dimerization of Ge is energetically favourable, forming symmetric Ge dimer, and the Te monolayer acts as a buffer layer, avoiding a buckling process of the Ge dimer. The subsequent dimer exchange process between Ge and Te atoms is also an exothermical process, in agreement with the surfactant effect of Te. Finally, we have considered a full monolayer of Ge on Si(001)/Te, Si(001)/Te/Ge - 2×1 reconstructed. The complete (layer) exchange between Te and Ge atoms, Si(001)/Ge/Te - 1×1 reconstructed, is also energetically favourable, reducing the total energy by 0.97 eV atom, also confirming the surfactant effect of Te atoms.

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References

[1] M.R. Bennett, C.J. Dunscombe, A.A. Cafolla, J.W. Cairns, J.E. MAcdonald, R.H. Willians, *Surf. Sci.* **380**, (1997) 178.

[2] S. Higushi, Y. Nakanishi, *J. Appl. Phys.* **71**, (1992) 4277.

[3] S.A. Yoshikawa, J. Nogami, C.F. Quate, P. Pianetta, *Surf. Sci.* **321**, (1994) L183.

[4] S. Di Nardo, L. Lozzi, M. Passacantando, P. Picozzi, S. Santucci, *Surf. Sci.* **331/333**, (1995) 569.

[5] M.R. Bennet, A.A. CAfolla, J.W. Cairns, C.J. Dunscombe, R.H. Willians, *Surf. Sci.* **360**, (1996) 187.

[6] S. Santucci, S. Di Nardo, L. Lozzi, M. Passacantando, P. Picozzi, *Surf. Sci.* **352/354**, (1996) 1027.

[7] S.R. Burges, B.C.C. Cowie, S.P. Wiks,P.R. Dunstan, C.J Dunscombe, R.H. Willians, *Appl. Surf. Sci.* **104/105**, (1996) 152.

[8] P. Hohenberg and W. Kohn, *Phys. Rev.* **B864**, (1964) 136.

[9] D. M. Ceperley and B. I. Alder, *Phys. Rev. Lett.* **45**, (1980) 566.

[10] J.P. Perdew and A. Zunger, *Phys. Rev.* B **23**, (1981) 5048.

[11] L. Kleinmann and D.M. Bylander, *Phys. Rev. Lett.* **48**, (1982) 1425, X. Gonze, R. Stumpf and M. Scheffler, *Phys. Rev.* B **44**, (1991) 8503.

[12] R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, (1985) 2471.

[13] R. Stumpf and M. Scheffler, *Comput. Phys. Comm.* **79**, (1994) 447.

[14] J. Neugebauer and M. Scheffler, *Phys. Rev.* B **46**, (1992) 16067.

[15] E. Fontes, J. R. Patel, F. Comin, *Phys. Rev. Lett.* **70**, (1993) 2790.

[16] J.-H. Cho, S. Jeong, M.-H. Kang, *Phys. Rev.* B **50**, (1994) 17139.

[17] S. J. Jenkins, G. P. Srivastava, *Surf. Sci.* **377-379**, (1997) 887.