

Defect-mediated carbon incorporation in the Si(001) surface: role of stress and carbon-defect interactions

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Abstract

We present a comparative theoretical study of carbon incorporation on the Si(001) surface with and without Si defects, such as parallel and perpendicular ad-dimers or dimer vacancies. The influence of different parameters such as surface reconstruction, local stress before and after carbon adsorption and carbon-defect interaction are investigated. We find that ad-dimers or dimer vacancies make carbon incorporation easier, which can be explained by taking the above parameters into account in a systematic and combined way. The energetic barrier found for the defect-free surface at the crossing of the second layer is substantially lowered or vanishes. The site located just below the defect (in the third or fourth layers in the ad-dimer and dimer vacancy cases, respectively) is favored, and the site located in the middle between two defects plays a particular role.

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1. Introduction

Carbon incorporation in the silicon matrix extends the range of electronic properties obtained using silicon alone, and opens exciting perspectives in the field of silicon based heterostructures. However, the size difference between carbon and silicon makes this incorporation difficult and only small amounts of carbon (a few percent) can be

introduced without giving rise to SiC precipitation. Thus an important issue is whether it is possible to improve the carbon penetration in silicon, particularly in the case of the technologically important Si(001) surface. Various theoretical studies have examined the structure and stability of substitutional carbon impurities in the proximity of the Si(001) surface. However the results have been rather controversial, as some model predict the formation of carbon clusters at the first and second surface layers, in the presence of missing Si dimers [1], other suggest penetration of carbon atoms in the third or fourth layers [2,3], whereas other studies indicate that both surface and subsurface

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carbon atoms should be present [4–11]. In an earlier first-principles study [9], in particular, we found that carbon atoms start to penetrate into the subsurface layers at rather low coverage ($\theta \sim 0.125$ ML), and that configurations with carbon atoms equally distributed between the surface and the α sites of the fourth layer are energetically favored, whereas a second layer location is highly unfavorable [9,10].

Si defects on Si(001), such as dimer vacancies [4] (DV) or ad-dimers [12,13] (AD) may play an important role in carbon penetration in the subsurface layers. These effects are not always taken into account in the proposed models. Investigating them systematically could help to clarify the above controversy. Moreover, acting on the surface defects, might improve carbon penetration in Si(001) and allow a better control of the carbon atom position in the subsurface layers. A few groups have considered dimer vacancies. According to Refs. [3,14], the most favorable location for carbon incorporation is the α site of the fourth subsurface layer, directly below the dimer vacancy. As the influence of ad-dimers on carbon incorporation on Si(001) had not been investigated to our knowledge, we recently proposed an energetic study on this subject [15]. The ad-dimers considered were either parallel (parAD) or perpendicular (perAD) to the dimer rows of the clean surface. We showed that AD presence makes carbon penetration in the subsurface layers easier. At low coverages ($\theta < 0.125$) carbon atoms are preferentially adsorbed in the third layer directly below an AD and the barrier to cross over to the second layer is strongly reduced (parAD case) or completely vanishes (perAD case). At higher coverage ($0.125 \leq \theta \leq 0.25$), configurations with part of the carbon at the surface and part in the third layer are favored. The results of this work parallel those of carbon incorporation in the case of a dimer vacancy (DV) [3,14], in which carbon is preferentially adsorbed in the fourth layer, just below the DV.

Here, we further examine the influence of Si defects on carbon incorporation on Si(001) by performing a systematic investigation of the role of various parameters, such as the position of carbon atom with respect to the surface layer (effect i), surface reconstruction (effect ii), local stress (effect

iii) and carbon-defect interaction (effect iv). Effects i and ii have been studied in the past [16,17]. Tersoff showed that the equilibrium solubility of carbon in silicon is increased by several orders of magnitude for the first four layers of the Si(001) surface [16]. This increased solubility results from two factors: first, the presence of the surface partially relieves the stress associated with the atomic size mismatch between C and Si (effect i); the second effect depends on the particular surface structure. In the case of the dimerized Si(001)- 2×1 surface, there are two inequivalent sites in the third and fourth subsurface layers: the so-called α sites, beneath the surface dimers, are under compressive stress and are thus favorable sites for a smaller atom such as carbon; the so-called β sites, located between dimers, are under tensile stress, and are thus highly unfavorable sites for carbon (effect ii).

In this paper we focus on effects iii and iv. We study a single carbon atom adsorption on the defect-free Si(001) surface, the Si(001) surface in the presence of a parAD or a perAD, and, finally, on the Si(001) surface with a DV. In this case, there are no C–C interactions that could modify the carbon adsorption sites [5,8,18,19]; the four effects under consideration are not perturbed by the C–C interactions and a more fundamental systematic study can be realized. In each case, a first-principles energetics study, an investigation of the local stress before and after carbon incorporation based on empirical interatomic potentials, and carbon-defect interaction calculations are performed.

2. Model

In our first-principles energetics study of carbon adsorption on the Si(001) surface with and without Si ad-dimers or dimer vacancies, we use an approach similar to the one presented in Ref. [9]. The calculations are performed in a plane wave-pseudopotential [20] approach within local density functional theory. Norm-conserving pseudopotentials and a kinetic energy cutoff $E_{\text{cut}} = 35$ Ry are used. The Si(001) surface is modeled by means of a periodically repeated slab of eight Si atom layers. We use a supercell containing eight silicon

atoms per layer, giving rise to four surface dimers, while the bottom of the slab is kept in a bulk-like configuration with the dangling bonds saturated by hydrogen atoms. The Si ad-dimers are located on the upper surface either in parallel (parAD) or perpendicular (perAD) direction with respect to the dimer rows (see Fig. 1). Carbon impurities are introduced in various substitutional adsorption sites of the surface and/or subsurface layers. The upper six layers of the slab, plus the ad-dimer, are relaxed using damped ab initio molecular dynamics [21], while the atoms of the bottom two layers and the lower hydrogen layer remain fixed. The vacuum layer thickness is 8 Å. Further details are given in Ref. [9].

Since we always incorporate a single carbon atom for each type of Si(001) surface—Si(001) without defect, Si(001) with ad-dimer, Si(001) with dimer vacancy—, we describe the energetics simply in terms of relative energies. We define the carbon-defect interaction energy as

$$E_{\text{int}} = E_{\text{ads}}(\text{carbon} + \text{defect}) + E_{\text{clean}} - E_{\text{ads}}(\text{carbon}) - E_{\text{ads}}(\text{defect}).$$

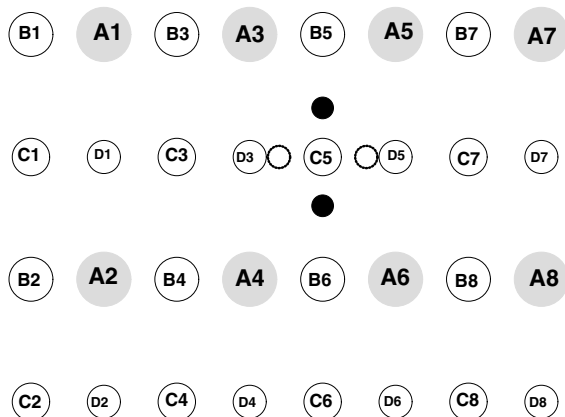


Fig. 1. Top view of the atomic arrangement along the diagonal of the $c(4 \times 4)$ cell in the ideal case (without dimer reconstruction). The atoms of the outermost four layers are indicated: A, B, C and D denote atoms of the first, second, third and fourth layers respectively. Atoms at increasing distance from the surface are represented by circles of decreasing size. The two black circles and, the two dashed circles indicate the parallel and perpendicular ad-dimer location respectively.

Here the various terms are total energies for: the clean defect-free surface (E_{clean}), the carbonate surface in presence of the defect ($E_{\text{ads}}(\text{carbon} + \text{defect})$), the carbonate surface without defect ($E_{\text{ads}}(\text{carbon})$) and the defected surface without carbon ($E_{\text{ads}}(\text{defect})$). Clearly, a positive (negative) E_{int} indicates repulsive (attractive) carbon-defect interaction.

Our density functional theory approach allows to calculate the total stress but not the local stress of interest in this work. The local stress before and after carbon incorporation is calculated via Monte Carlo simulations, in the framework of an empirical formalism based on the interatomic Tersoff's potentials [22] for multicomponent systems. This approach has been successfully used in similar contexts, for instance in $\text{Si}_{1-x}\text{Ge}_x\text{C}_x$ alloys [23]. The use of this empirical approach to analyze our first-principles results is justified by the fact that the relative carbon incorporation energies obtained with Tersoff's potentials are in qualitative agreement with the ab initio results. The Monte Carlo simulation cells consist of 16 layer slabs, each containing 256 Si atoms. The top layer is reconstructed in the usual 2×1 dimer configuration. The calculations are performed at 300 K.

The local stress can be viewed as an atomic hydrostatic compression (tension), defined by $\sigma_i = -dE_i/d\ln V \sim p\Omega_i$, where E_i is the energy of atom i (as obtained by decomposition of the total energy into atomic contributions; this is readily done in the present empirical potential approach), and V is the volume. Division by the appropriate atomic volume Ω_i converts into units of pressure [17,24].

3. Defect-free Si(001) surface

We first consider the incorporation of a single carbon atom in the defect-free Si(001) surface. The carbon atom is successively incorporated in substitutional sites of the first, second, third, fourth and fifth silicon layers. For each layer, the energy of the most stable site is reported in Fig. 2(a). Carbon adsorption at the surface is slightly favored (agreement with effect i) and the α sites of the third and fourth layers are clearly more stable

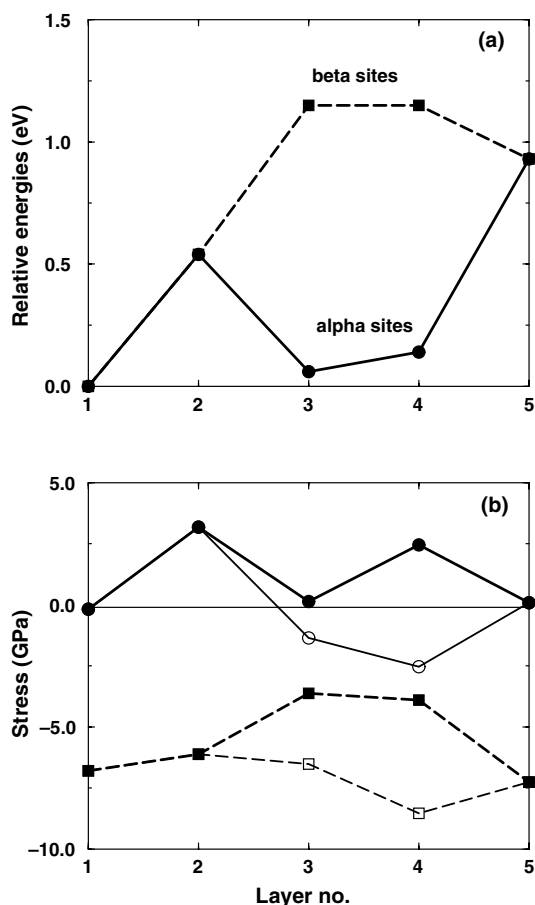


Fig. 2. (a) Relative energies of configurations involving a single substitutional carbon atom on the defectless Si(001) surface versus the layer number. The zero of energy corresponds to the most stable configuration. (b) Local stress before (full line) and after (dashed line) a single carbon incorporation on the defectless Si(001) surface versus the layer number. Layer 1 corresponds to the surface.

than the β sites of the same layers (agreement with effect ii), but these two effects do not explain the presence of a barrier ($E_b = 0.54$ eV) at the crossing of the second layer.

Let us now investigate (see Fig. 2(b)) the local stress before and after carbon incorporation (effect iii). Before carbon incorporation, the compression is maximum in the possible adsorption sites of the second and fourth layers. We therefore expect preferential adsorption in these sites, which is not the case since the first and the third layers are favored in the energetics study. In the presence of

carbon, the local stress is clearly modified. As a general finding, we observe that carbon atoms experience large local tensile stresses because are stretched to fit in the surrounding Si lattice, having larger dimensions. The α sites of the third and fourth layers become by far the less tensile ones (-3.63 and -3.90 GPa respectively), followed by the second and first layer sites (-6.12 and -6.80 GPa) and the β sites (-6.52 and -8.54 GPa). The crystal lattice will therefore be much more bent under carbon adsorption in the second layer than in the third or fourth layers. This favors carbon incorporation in the α sites of the third and fourth layers rather than in the second one, the third layer being the most likely. In the same way, the very tensile β site of the third and fourth layers, as well as that of the fifth layer, are less favored than the α type and the second layer ones.

Let us now examine carbon incorporation in the first layer site. Apart from the β sites of the third and fourth layers, this site has become the most tensile one and is, at first sight, the least likely. But its surrounding is very different: it has only three saturated bonds, the relaxation is easier, and its influence on the crystal lattice weaker. The *ab initio* calculated Si–C distances are shorter in the surface (1.788 – 1.841 Å) than in subsurface layers (1.891 – 1.970 Å). This indicates a stronger bond, and so we have a gain in chemical energy which compensates for the higher stress. These considerations may explain an easier carbon incorporation at the surface than in subsurface layers.

We conclude that the stress investigation of the carbon-free surface alone does not allow one to explain the results of the *ab initio* energetics study. On the other hand, examining the stress of the same sites before and after carbon incorporation emphasizes effect iii: it is the effect of the carbon atom on the adsorption site and its impact on the lattice that first drive single carbon incorporation on the undefected Si(001) surface.

4. Si(001) surface plus an ad-dimer

In order to investigate the influence of ad-dimers, we now consider the same type of config-

urations as already described in Section 2, but in the presence of a parAD or a perAD, and with the carbon atom as close as possible to the ad-dimer. The calculated relative energies are reported in Figs. 3(a) and 4(a) and compared to a single carbon adsorption on the defectless Si(001) surface (Fig. 2(a)). In the presence of a parAD, the α sites are again more favored than the β sites, as expected from the surface reconstruction (effect ii). But, in disagreement with effect i, carbon incorporation at the surface is no more likely, the third layer is now clearly favored, and the barrier at the crossing of the second layer is substantially lowered.

Results for the local stress before and after carbon incorporation (effect iii) are reported in Fig. 3(b). Before carbon incorporation, the compressive stress increases from the first to the third layer, and slightly decreases in the fourth layer. After carbon incorporation, the same tendency—considerably enhanced—is observed. Following this local stress study, we would expect carbon incorporation at adsorption sites in the second, third, and fourth layers to become more likely. This effect does not allow one to explain the presence of a barrier at the crossing of the second layer predicted by the energetics study.

Let us now turn to the carbon-defect interaction (Fig. 5). In the case of a parAD, this interaction decreases from the first to the third layer, favoring incorporation in the third layer with respect to the surface one. It also favors carbon adsorption into the second layer with respect to the surface ($\Delta E_{\text{int}1-2} \sim 0.45$ eV) but is not sufficient to suppress the barrier at the crossing of the second layer whose height was 0.54 eV in the defectless surface case. The barrier height (0.12 eV) is now substantially decreased but does not vanish. Here the carbon-defect interaction plays a major role by decreasing the barrier and favoring carbon incorporation in the third layer as observed in the energetics study.

In the perAD case, the relative energy curve (Fig. 4(a)) shows similar—but enhanced—tendencies to the case of a parAD (Fig. 3(a)). The barrier at the crossing of the second layer now vanishes, and adsorption in the third layer is again favored. Carbon incorporation in subsurface layers is easier

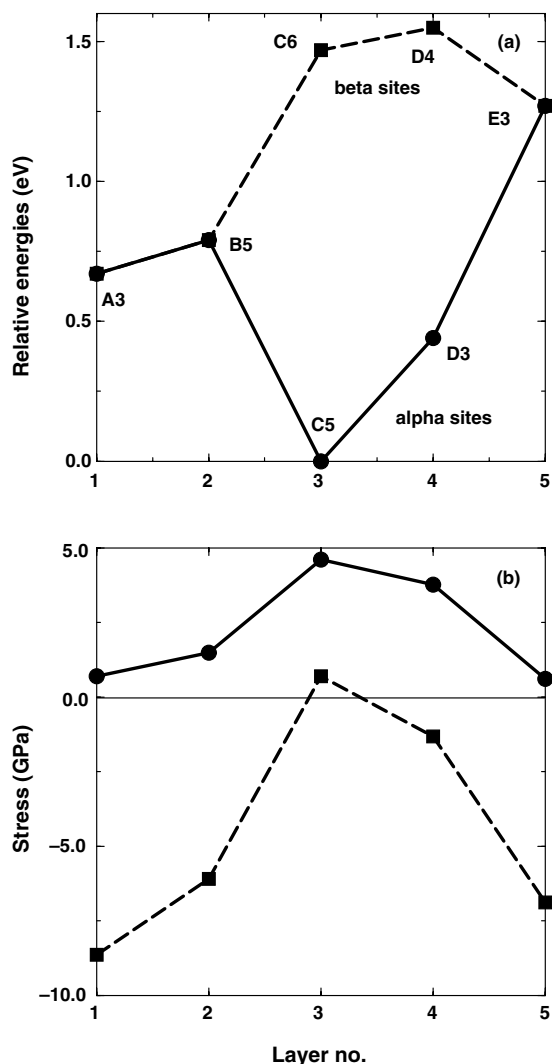


Fig. 3. (a) Relative energies of configurations involving a single substitutional carbon atom on the Si(001) surface plus a parAD versus the layer number. The zero of energy corresponds to the most stable configuration. (b) Local stress before (full line) and after (dashed line) a single carbon incorporation on the Si(001) surface plus a parAD versus the layer number. Layer 1 corresponds to the surface.

up to the third layer. The perAD presence acts against effect ii even more than the parAD one. How can one explain these modifications? The local stress study (Fig. 4(b)) indicates, before carbon incorporation, more compressive stress in the second and fourth layers (that could help the vanishing of the barrier) but, after carbon

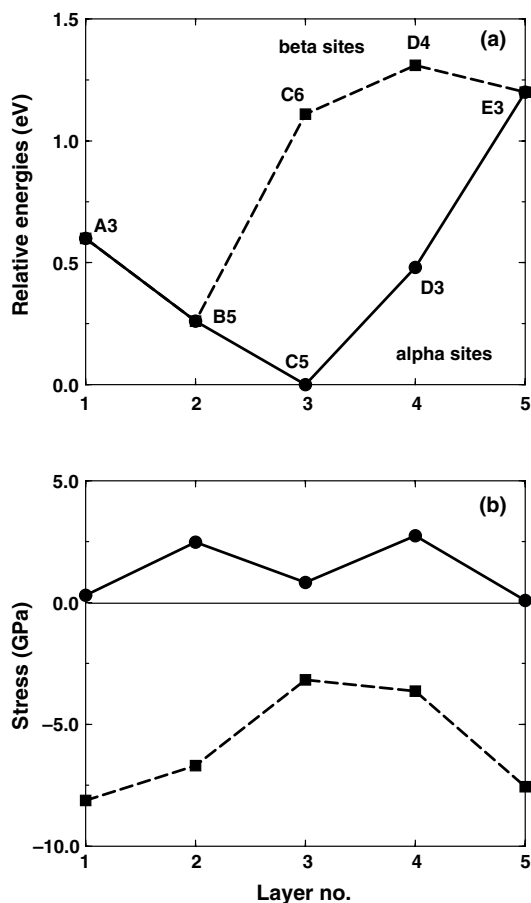


Fig. 4. (a) Relative energies of configurations involving a single substitutional carbon atom on the Si(001) surface plus a perAD versus the layer number. The zero of energy corresponds to the most stable configuration. (b) Local stress before (full line) and after (dashed line) a single carbon incorporation on the Si(001) surface plus a perAD versus the layer number. Layer 1 corresponds to the surface.

incorporation, we again find analogous tendencies, slightly attenuated, to the parAD case. This local stress favors carbon incorporation in the third layer but does not allow understanding of the vanishing of the barrier. The carbon-defect interaction energy (Fig. 5) which is particularly attractive in the second layer ($\Delta E_{\text{int1-2}} \sim 0.90$ eV; $\Delta E_{\text{int1-3}} \sim 0.25$ eV) clearly explains the vanishing of the barrier, but is not sufficient to favor carbon adsorption in the second layer rather than in the third or first layers.

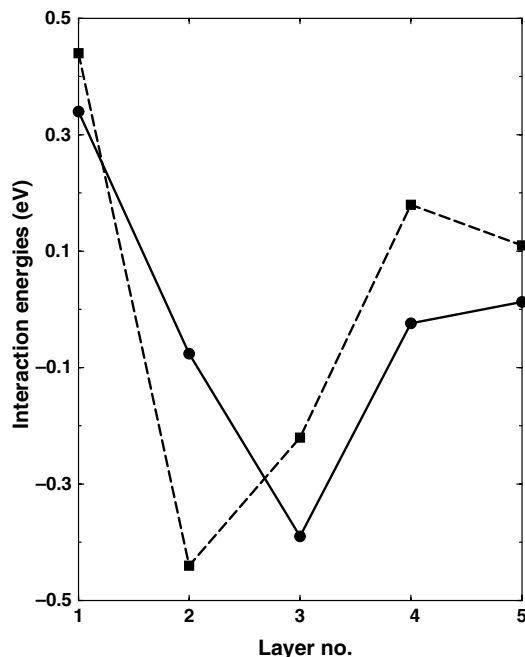


Fig. 5. Carbon-defect interaction energies versus the layer number in parAD (full line) and perAD (dashed line) presence on Si(001). Layer 1 corresponds to the surface.

We conclude that in parAD and even more in perAD presence, it is mainly the carbon-defect interaction (effect iv) in addition to the local stress (effect iii) that makes carbon penetration in the subsurface layers easier. We also notice that before carbon incorporation, the AD orientation (parallel or perpendicular to the dimer rows) influences the subsurface local stress: in the perAD case, the local stress of the third layer site is less compressive than in the parAD case. It roughly parallels that of the defectless surface. A possible explanation is that the perAD is located in epitaxial position. After carbon incorporation, we find analogous behavior, enhanced in the parAD case.

5. Si(001) surface with a dimer vacancy

In the case of a single carbon incorporation in the Si(001) surface with a DV, recent works [3,14] agree with carbon preferential adsorption in the subsurface layers. We therefore limit our study to

Table 1

Relative energies (ΔE), interaction energies (E_{int}), stress before and after carbon incorporation, for configurations involving one substitutional carbon atom, located in the third or fourth layer, in a $c(4 \times 4)$ cell with one DV

Carbon position	ΔE (eV)	E_{int} (eV)	Stress before (GPa)	Stress after (GPa)
(3)	0.70	0.10	3.22	−3.79
(4)	0.00	−0.68	4.90	−3.93

$\Delta E = 0$ corresponds to the most stable configuration. Notation (3) and (4) refer to the third and fourth layer sites just below the DV.

the third and fourth subsurface layers, and compare our results to the defect-free Si(001) subsurface and with AD cases. The results of the first-principles energetics calculation, the local stress before and after carbon incorporation and the carbon-defect interaction are reported in Table 1 and Fig. 6. Our energetics study shows that carbon location under the DV in the fourth layer is largely favored, in agreement with Refs. [3,14]. The local stress is more compressive in the fourth layer before carbon incorporation and in the third layer after carbon incorporation. Following this local stress study alone, incorporation in the third layer should be slightly favored, but the carbon-defect interaction energy, largely more attractive for carbon adsorption in the fourth layer than in the third layer (Table 1), stabilizes the carbon atom in the fourth layer. Here again, our study emphasizes the role of the carbon-defect interaction.

6. Conclusions

In order to facilitate the comparison between the influence of the different investigated Si defects on carbon incorporation, we focus on a single figure (Fig. 6), showing the calculated relative energies for the different adsorption sites of the third and fourth layers. Only α sites, clearly more favorable than β sites, are considered. In the defect-free surface case, all sites of the same layer are equivalent. Si defects such as AD or DV break the symmetry and the inequivalent sites have to be investigated. In the AD case, the sites located directly below the AD in the third layer are the most

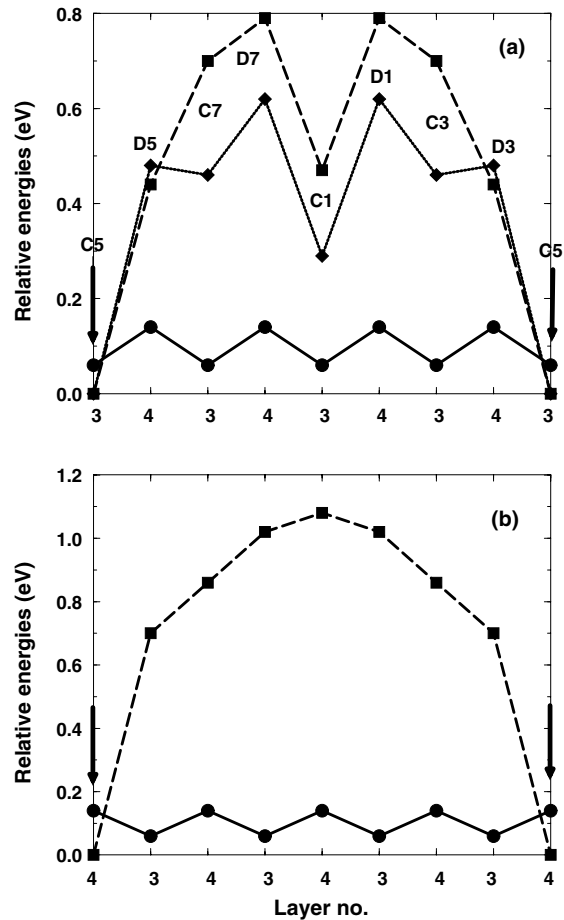


Fig. 6. (a) Relative energies of configurations involving a single substitutional carbon atom on the defectless Si(001) surface (full line) and on Si(001) in presence of a parAD (dashed line) or a perAD (dotted line) versus the layer number (third or fourth layer). The arrow indicates the parAD or perAD locations in the unit cell. All sites of a same layer are considered in order of increasing distance to the perAD or parAD. (b) The same in the case of the defectless Si(001) surface (full line) and the Si(001) surface with a DV (dashed line). The zero of energy corresponds to the most stable configuration.

stable ones, and we find a metastable site in the third layer, in the middle between two ADs. In the DV case, the only stable site is located in the fourth layer, below the DV; the site in the middle between two DVs in the fourth layer is here the less favored one.

It appears that the results for the DV and AD cases show similar trends, since in both cases the

site located just below the defect is favored, and the site located in the middle between two defects plays a particular role (metastable in the AD case, the less likely one in the DV case). As the periodicity is modified, there is only one preferential site per unit cell in the presence of a Si defect, whereas there are four equivalent sites in the third or fourth layers of the defectless surface. On the other hand, the local stress modification and, especially, the carbon-defect interaction facilitates in all cases the carbon penetration in Si(001).

In summary, we have analyzed the influence of ad-dimers and dimer vacancies on carbon incorporation in Si(100) in terms of various parameters, including the position of carbon atom with respect to the surface layer, surface reconstruction, the local stress before and after carbon adsorption and the carbon-defect interaction. We have found that these silicon defects facilitate carbon incorporation and that it is mainly the carbon-defect interaction in addition to the local stress that makes carbon penetration in the subsurface layers easier. Finally, acting on the surface defects might improve carbon penetration in Si(001) and allow a better control of the carbon position in the subsurface layers.

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