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Adatoms and vacancies on the diamond(111) surface

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Abstract. – First-principles total-energy and band-structure calculations are performed for a series of 2×2 adatom structures and vacancies on the diamond(111) surface. The optimized geometries are related to band structures with narrow or vanishing gaps. In contrast to silicon and germanium, we find that adatoms and vacancies on the diamond surface are energetically less favourable than the relaxed unreconstructed surface.

For both homoepitaxial and heteroepitaxial growth the thorough understanding of the low-index surfaces of diamond is essential. This holds especially for the C(111) face. Adatoms and vacancies are important elements to characterize homoepitaxial growth.

After hydrogen desorption the C(111) surface shows a 2×2 LEED pattern that is commonly interpreted to arise from a superposition of three rotated 2×1 domains [1]. Such surface structures also seem to be observable in case of polycrystalline diamond films grown by chemical-vapour deposition (CVD) [2]. In addition to the 2×1 reconstruction Si(111) and Ge(111) surfaces possess 7×7 and $c(2\times8)$ reconstructions, respectively. Such rough reconstructions have not been found in the diamond case. The only idea for an explanation is related to the possibility of a surface phonon softening which occurs for Si and Ge but not for diamond [3]. The dimer-adatom-stacking fault (DAS) model [4] for the 7×7 structure as well as the dimer-chain model [4], [5] or the adatom model [6] for the $c(2\times8)$ surface contain adatoms as the most important reconstruction elements. An adatom cluster consists of one adatom bonded to three underlying atoms and can occur in regions with different stacking [4], [5] or equal stacking [6]. In the DAS model also corner holes appear. A first step towards such reconstruction elements could be vacancies. The energetics of the considered structural elements may help to understand why a rough reconstruction does not occur at the C(111) face.

In this paper we present first-principles calculations of the energetics of carbon atom adsorption or desorption as well as the structural and electronic properties of adatoms and vacancies on the C(111) surface. The calculations are based on density-functional theory in local-density approximation and the plane-wave pseudopotential method [7]. The Bachelet-Hamann-Schlüter–type pseudopotentials are softened [8]. This allows a restriction of the

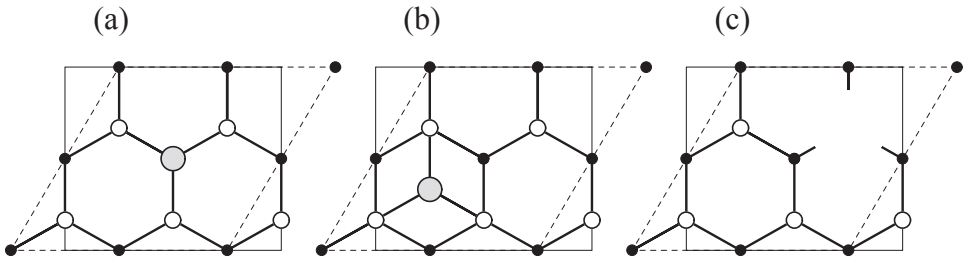

Fig. 1. – Adatoms in T_4 (*a*) and H_3 (*b*) sites as well as a vacancy geometry (*c*) forming 2×2 lattices on C(111) surfaces (top view). The atoms are indicated by circles (first layer) or dots (second layer). Adatoms are shaded. Rectangular (hexagonal) cells are indicated by solid (dashed) lines.

plane-wave cut-off to 42 Ry. In order to simulate the surfaces we use the repeated-slab method. Each slab consists of eight atomic layers of carbon and a vacuum region equivalent in thickness. One surface of the slab is terminated by hydrogen. To account for artificial electric-dipole fields due to the asymmetry of the slab a dipole correction [7] is made. We assume a 2×2 translational symmetry parallel to the surface. Both hexagonal (h) and rectangular (r) 2×2 surface cells are considered. The **k**-space sampling is performed with sixteen (six) special points in the rectangular (hexagonal) surface Brillouin zone (BZ). In the rectangular case a larger number of **k** points have been used since the considered structures are semimetallic. In order to determine the equilibrium positions the atoms in the first four atomic layers and the adatom are allowed to relax until the Hellmann-Feyman forces vanish. Simultaneously the electronic wave functions are brought to self-consistency by means of a steepest-descent algorithm [7].

There is now general agreement that the atoms in the ideal C(111)2×1 surface prepared after annealing of (111)-orientated diamond crystals possess one dangling bond before reconstruction and rearrange to form π-bonded Pandey chains [9], [10]. Considering adatoms and vacancies we start from a single-dangling bond surface. Dangling-bond reduction is the driving force for adsorption of additional atoms on top of the single-dangling bond surface. The study of the adsorption within 2×2 surface cells results in an adatom coverage of $\frac{1}{4}$. Each adatom is bonded to three surface atoms below, resulting in a net reduction of two dangling bonds per 2×2 unit cell. Besides the adatom one atom in the original topmost surface layer, the so-called restatom, keeps a dangling bond. As indicated schematically in fig. 1, threefold-coordinated adatoms may occupy two types of sites on diamond(111) surfaces. The hollow (H_3)-site and on-top(T_4)-site geometries depend on whether the substrate atom below the adatom is found in the fourth or second layer, respectively. $\sqrt{3}\times\sqrt{3}$ reconstructions induced by adatoms are not considered here. Their adatom coverage of $\frac{1}{3}$ is too large. Since no restatom occurs, one dangling bond remains per unit cell. Consequently, the $\sqrt{3}\times\sqrt{3}$ face leads to a half-filled surface band [11] and should therefore be energetically unfavourable. To study the influence of the symmetry of the arrangement of adatoms and restatoms we consider both rectangular (r) and hexagonal (h) surface unit cells. Vacancies (V) are only investigated in hexagonal unit cells which could allow the formation of benzene-like ring structures. Vancancies lead to three additional dangling bonds. Together with the dangling bonds of the three atoms remaining in the surface layer, we end up with an even number of dangling bonds and electrons in a unit cell.

The energy gains of the investigated structures with respect to the relaxed 1×1surface unit cell are given in table I. For comparison we also cite values for Si and Ge and compare with

results for the Pandey π-bonded chain reconstructions. The values for the diamond adatom structures indicate that the relaxed T_4 geometries in hexagonal and rectangular 2×2 unit cells are the most favourable structures investigated. However, there are no energetically significant differences to the three other structures considered here. The fact that the top-site covering has the lowest energy is in agreement with results for Si and Ge [12], [13]. In case of diamond as well as for Si and Ge (111) surfaces Pandey π-bonded chains give rise to lower surface energies than adatoms in 2×2 unit cells. The energetical difference is very small for Si and Ge, where π-bonded chains are only metastable, in contrast to the diamond case. A further pronounced difference between diamond on the one hand and silicon and germanium on the other hand concerns the energetical order of the adatom structures with respect to the relaxed 1×1 surface: While the presence of adatoms lowers the energy in case of Si and Ge, it is unfavourable for diamond(111). The energy gain due to the relaxation of the clean diamond(111) surface, which varies only by about 0.01 eV with the different **k**-point sets used, is larger than the values for the T_4 faces by 0.10 eV (h) or 0.11 eV (r). This indicates that the relaxed C(111)1×1 surface does not transform spontaneously into an adatom-covered face. The reduction of the number of dangling bonds indeed lowers the band structure energy contribution to the total energy. However, in contrast to Si and Ge, the strain in the backbonds due to displacements of adatom-terminated first-layer atoms and the restatom limits the effective energy gain remarkably. For diamond the strain is larger because of the stronger covalent bonds. (The bulk modulus of diamond is about 5 (6) times larger than that of Si (Ge).)

The relaxation of the adatom and vacancy geometries mainly involves displacements of atoms in the first atomic layers. The nearest neighbours to the adatom move closer together, and in the T_4 case the second-layer atom beneath the adatom is displaced downward. However, the effect is smaller than in silicon. The bond lengths between adatoms and surface atoms are larger than the diamond bulk bond length (cf. table I). In the T_4(r) case the stretching

TABLE I. – *Energy gain E per* 1×1 *surface cell* (*relative to the relaxed* $1\times$ *surface*), *characteristic averaged bond lengths d between the adatom and surface atoms* (*or first- and second-layer atoms in case of the vacancy*), *and distances of adatom and restatom D. d and D are given in units of the ideal bulk bond length. For comparison we also cite values for* Si *and* Ge *and compare with results for the Pandey* π*-bonded chain reconstruction.*

Structure	E(eV)	*d*	*D*
C(111)			
T_4(r)	−0.11	1.07	1.99
H_3(r)	−0.14	1.05	1.97
T_4(h)	−0.10	1.06	1.97
H_3(h)	−0.12	1.05	2.02
V(h)	−0.16	0.93	—
Pandey (ref. [10])	0.83	—	—
Si(111)			
T_4(h) (ref. [13])	0.27	1.05	1.91
Pandey (ref. [13])	0.28	—	—
Ge(111)			
T_4(h) (ref. [13])	0.20	—	—
T_4(h) (ref. [14])	0.27	—	—
Pandey (ref. [14])	0.28	—	—

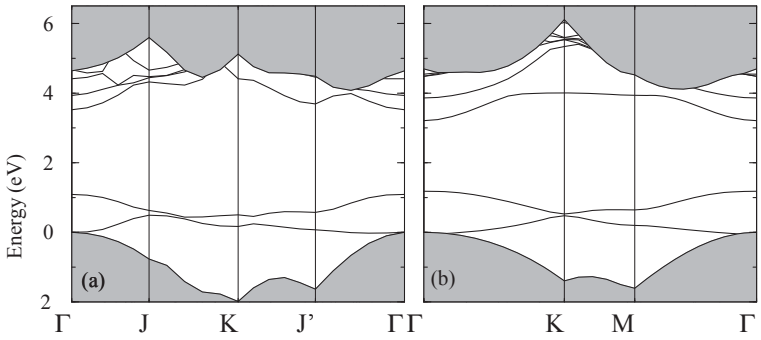

Fig. 2. – Surface bands for *a*) the T_4(r) system and *b*) the T_4(h) system. The Fermi energy is pinned by or lies between the two surface bands in the lower part of the fundamental gap.

amounts to about 7%. Roughly the same distance is observed to the atom in the second layer below the adatom. The bond of this atom to the next layer, however, is remarkably shortened by about 6%. The distance D of the adatom and the restatom (table I) remains, with about twice the ideal bulk bond length, rather large. In the case of the vacancy there is a tendency to displace the second-layer atoms with one dangling bond (first-layer atoms) towards the surface (substrate). The bond lengths between these atoms are shortened (cf. table I). However, we find no indication that the three first-layer atoms and the three second-layer atoms with one dangling bond form a benzene-like ring structure surrounded by three vacancies.

The band structures of the two T_4 adatom structures are shown in fig. 2. Several surface bands appear in the projected fundamental gap of diamond. For rectangular symmetry the surface bands related to the dangling bonds of adatom and restatom come close together and form a slightly semimetallic band structure with the band extrema, at which electrons and holes appear, along the JK line. In the hexagonal case these orbitals give rise to occupied and empty surface bands separated by a tiny direct energy gap at K. Several empty surface bands occur close to the projected bulk conduction bands. The slightly semimetallic character of the T_4(r) surface may explain why hexagonal cells are more favourable than rectangular ones. The findings are different from those for silicon [13], where occupied and empty surface bands are close to the bulk valence- and conduction-band edge, respectively. The calculated bands suffer from the well-known underestimation of excitation energies within DFT-LDA. Self-energy corrections to the band structure may open or widen the energy gap as shown for the C(111) 2×1 surfaces in ref. [15]. However, the relative proximity (compared to Si) of the occupied and unoccupied surface bands in the lower part of the bulk band gap should be conserved. Geometric structures and total energies are usually reliably calculated within DFT-LDA and are therefore not expected to change significantly due to self-energy corrections in contrast to the excitation energies.

In order to understand the origin of the surface bands the wave function squares of the two midgap surface bands at the J' point are plotted for the top-site adatom structure in fig. 3. Similar to the findings for silicon [13], the lowest empty state is mainly localized on top of the adatom but also somewhat in the $(1\bar{1}0)$ chain of backbonds below. However, in contrast to silicon, one also observes some localization on top of the rest atom. The highest occupied state exhibits a complementary behaviour. The roles of adatom and restatom are changed. The two states look like combinations of dangling bonds at adatom and restatom and indicate that the charge transfer between adatom and restatom is smaller than in case of Si.

For a lateral 2×2 superlattice of vacancies in a hexagonal surface unit cell many bands with a strong dispersion are observed within the projected fundamental gap. They are associated with

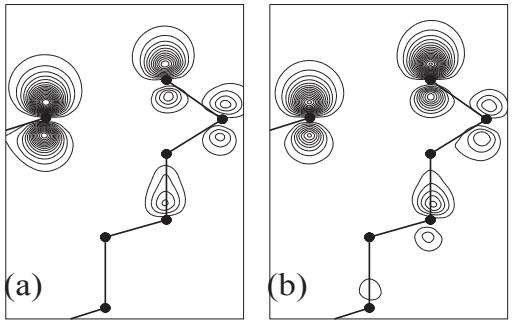

Fig. 3. – Contour plots of the wave function square for the two midgap surface states at J'. *a*) Occupied state and *b*) empty state. The figures show cross-sections on a $(1\bar{1}0)$ plane passing through adatom and restatom.

the dangling bonds of three atoms in the second atomic layer and the three atoms remaining in the first atomic layer. In each case a second-layer and a first-layer atom form a pair of first-nearest-neighbour atoms with a dangling bond and therefore dimers with bonding and antibonding combinations of dangling-bond states. However, the interaction of the three dimers within one unit cell as well as between neighbouring unit cells gives rise to a strong interaction of their states. Nevertheless the vacancy-covered surface exhibits a small energy gap in contrast to the observations for silicon [16].

In summary, we have performed *ab initio* calculations of four 2×2 adatom-covered C(111) surfaces and one surface where each fourth atom is missing in a hexagonal 2×2 unit cell. We have calculated surface energies, reconstructed geometries, and surface band structures. The nonideal surface structure with the lowest energy is a T_4 adatom geometry rather independent of the rectangular or hexagonal translational symmetry. We observe energy gains that are slightly lower than that for the relaxation of an ideal surface. Consequently, we conclude that adatoms or vacancies play a less pronounced role in stabilizing the diamond(111) surface compared to the Si or Ge case. This is probably due to the large energy loss upon bond stretching for diamond and may explain why no rough surface reconstructions with adatoms and holes or walls have been found for diamond.

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