

Diamond (111) and (100) surface: ab initio study of the atomic and electronic structure

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Abstract

Within the framework of density-functional theory in local-density approximation (DFT-LDA) we perform first-principles calculations for the atomic and electronic structure of diamond surfaces. The electron–ion interaction is described by a soft non-local carbon pseudopotential. For the C(100) surface we find a 2×1 reconstruction of symmetric dimers to be energetically favourable. For the C(111) surface we compare the surface energies of various reconstructions. In case of the single-bond (one-dimensional) 2×1 reconstructed cleavage face we find the π -bonded chain model to be lowest in energy, whereas at the triple-bond (three-dimensional) face a $(\sqrt{3} \times \sqrt{3})R30^\circ$ adatom-like model is similar in energy to the 2×1 single-chain model. For the equilibrium geometries we determine band structures and ionization energies.

Keywords: Diamond; Surface structure; Band structure calculations

Because of the increasing importance of carbon modifications in many technological applications, there has been a growing interest in their surface morphology over the last decade. Recent advances in thin film growth by chemical vapour deposition (CVD) have initiated renewed interest in the low-index surfaces of diamond, especially the (111) and (100) surfaces. Nevertheless, experimental knowledge of the diamond surface remains very poor because of substantial difficulties with techniques such as scanning tunnelling microscopy (STM) caused by the insulating character of the surface.

Parallel to developments of experimental techniques, ab initio methods have been proven to provide a powerful tool for determining the exact ground-state properties of many materials. In particular, fully self consistent calculations using density-functional theory in local-density approximation (DFT-LDA) can give a rather clear picture of the atomic and electronic structure.

Despite several theoretical investigations at various levels of sophistication, there are still uncertainties in the interpretation of the rare experimental data for the diamond surface. From a theoretical point of view it is very tempting to draw straightforward conclusions from the well established surface features of the other group IV elements Si and Ge to the diamond surface. However,

extensive theoretical investigations are difficult for carbon because of the extremely high number of plane waves necessary to treat the tightly bounded wave functions in large unit cells which are used to simulate surfaces.

The 2×2 structure of the C(111)-cleavage plane seen by low-energy electron diffraction (LEED) is now well established [1,2]. It occurs on annealing at about 1000 K from the hydrogen-passivated 1×1 -cleavage surface. The similarity of angle-resolved photoemission (ARPES) data [3–5] with those for Si [6] and Ge [7] suggests that it consists of 2×1 rotational domains with π -bonded chain reconstruction as first proposed by Pandey. This model is also supported by ion-scattering experiments [8]. Nevertheless, there remain open questions about the exact atomic positions and the electronic structure. From electron-energy loss spectroscopy (EELS) there is strong indication of a gap of approximately 2 eV along the JK direction in the surface-Brillouin zone (SBZ) [9]. This is interpreted as arising from either buckling of the surface atoms or dimerization of the surface chain [10–12].

On the theoretical side first-principles calculations using a self-consistent LCAO approach to DFT found undimerized π -bonded chains to be lowest in energy at the (111) surface [11]. However, recent molecular-dynamics DFT-LDA simulations obtain a dimerization of 1.4% in the chain and the opening of a gap of 0.2...0.3 eV near J [13]. Many-body quasi-particle computations using the results of [13] and [11] strongly support the

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Table 1

Reconstruction energy $\Delta E/N_{\text{sur}}$, surface-formation energy E_{sur} , ionization energy I , characteristic-bond length d (dimer-bond length etc.) and deviation to the bulk-like bond length Δd for the energy-minimum structures on the diamond surfaces

Surface	Reconstruction model	$\Delta E/N_{\text{sur}}$ (eV)	E_{sur} (eV)	I (eV)	d (Å)	Δd (%)
C(111)1 × 1, 1D	Ideal surface	0.00	6.53	5.7	1.53	0.0
C(111)2 × 1, 1D	π -bonded chain	−1.39	5.13	5.3	1.42	−7.2
	π -bonded molecule	−0.72	5.80	5.3	1.35	−11.8
C(111)2 × 1, 3D	Seiwatz single-chains	−1.92	8.33	6.0	1.45	−5.3
C(111)($\sqrt{3} \times \sqrt{3}$)R30°	H-site trimer	−1.73	8.58	4.9	1.38	−9.7
C(100)2 × 1	Ideal surface	0.00	9.76	7.9	1.53	0.0
	Symmetric dimer	−1.60	8.15	5.9	1.36	−11.1

dimerized π -bonded chain model giving rise to a gap of 1.7 eV, roughly explaining the EELS measurements [14].

For the C(111) triple-bond surface there has been some evidence from STM for the existence of a ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction of hollow (H)-site trimers on CVD grown polycrystalline films [15,16]. Other theoretical work proposes a 2 × 1 single-chain structure with geometrical and electronic properties similar to the π -bonded chain model which could explain at least some of the experimental data available so far [12].

In the case of the C(100) surface the experimental situation is still very undeveloped. Only the 2 × 1 structure of the surface is well established by LEED studies [17] and STM [15,18]. Several independently performed self-consistent DFT-LDA pseudopotential computations support a structure with symmetric dimers in the 2 × 1 unit cell [19–21].

We present results of fully self-consistent ab initio pseudopotential calculations within DFT-LDA. The exchange and correlation of the electron gas is described by a Ceperley–Alder-like treatment of the homogeneous electron gas. The electron–ion interaction is incorporated by use of a soft fully separable Kleinman–Bylander C pseudopotential [22]. The k -space integration is replaced by a summation over weighted special points in the irreducible part of the SBZ. The wave functions are expanded in plane waves up to a cut-off energy of 42 Ry. This cut-off has been proven to allow a reliable description of diamond-bulk properties such as equilibrium-lattice constant, band gap, total energy Γ (TO)-phonon frequency and bulk modulus. For energy minimization with respect to the atomic and electronic degrees of freedom, a Car Parrinello scheme implemented in a computer code by Stumpf and Scheffler [23] is used. The surface is modelled by repeated slabs of 12 atomic layers and a vacuum region equivalent in thickness. The five uppermost layers are allowed to relax on total energy and Hellmann–Feynman forces minimization.

The results are summarized in Table 1. The related atomic structures are presented in Fig. 1. The minimum-energy configurations of all C(111) one-dimensional (1D) surface reconstructions are characterized by the formation of surface π -bonds. This is in contrast to the Si and Ge surfaces where the energy gain on reconstruction is always due to single bonding and charge transfer accompanied by a buckling of the surface atoms. The structure lowest in energy in the 2 × 1 unit cell is the π -bonded chain structure (Fig. 2). The energy gain due to this structure formation is 1.39 eV per surface atom compared with the ideal bulk terminated surface. Dimerization of the chain and significant buckling always tend to increase the total energy in contrast to other DFT-LDA results [13] which favour a dimerized chain. However, the observed undimerized chain does not explain the opening of a gap in the electronic-band structure along JK , at least within the DFT-LDA framework. The surface states at J are

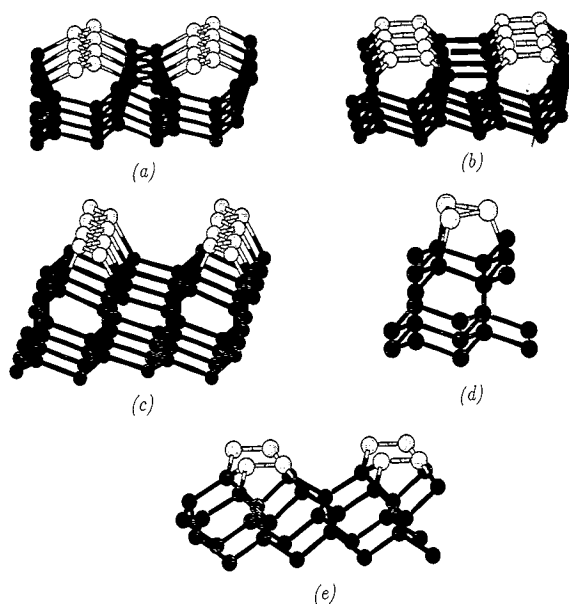


Fig. 1. Perspective view of the structures for (a) the π -bonded chain, (b) the π -bonded molecule model on the C(111) 1D surface, (c) the single-chain, (d) the hollow(H)-site trimer model on the C(111) 3D surface, and (e) the symmetric-dimer model on the C(100) surface.

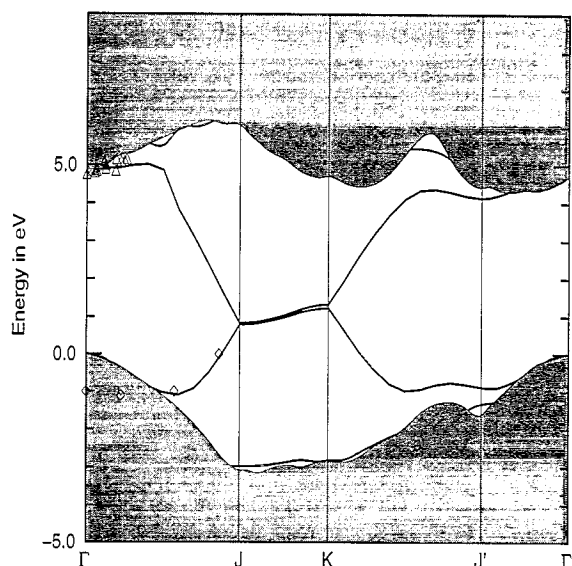


Fig. 2. Surface bands and projected bulk-band structure (shaded) of the π -bonded chain model. Experimental data from ARPES are shown for comparison, $\diamond$ [3], $\triangle$ [4].

nearly degenerated and the surface appears to be metallic. The π -bonding of the surface states is clearly visible along ΓJ exhibiting the 1D character of the undimerized chain. In good agreement with the ARPES data from [3], the occupied-surface state becomes resonant near Γ lying approximately 1 eV below the valence-band maximum (VBM). The agreement with the data from [4] is somewhat fortuitous because of the underestimation of the position of the unoccupied states due to the use of LDA balanced by the overestimation due to the slab-related particle-in-the-box effect.

Another 2×1 structure, the π -bonded molecule structure has been found to be about 0.7 eV per surface atom higher in total energy and therefore represents another metastable minimum [24]. The surface states exhibit π -bonding character opening a gap of around 3.5 eV along JK but show only weak agreement with the ARPES data near Γ .

On the C(111) 3D surface we found the single-chain structure in the 2×1 unit cell to be lowest in energy and to form π -bonded adatom chains similar in atomic and electronic structure to the 1D chains but with a somewhat smaller band splitting along Γ . This hints at a semi-metallic surface and could provide an explanation for the EELS data. Slightly higher in total energy (approximately 0.2 eV per surface atom) is a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure forming adatom-like trimers above a hollow(H)-site position in the sublayer. The Fermi level is pinned at a half-filled band roughly in the centre of the gap of the projected bulk-band structure. Therefore the surface is metallic. The trimer is asymmetric with two bond lengths shortened to 1.38 Å and a slight downwards buckling of the enclosed atom of 0.1 Å.

For the C(100) surface various structures such as $c/p(2 \times 2)$ and 2×1 have been tested. They all relax to a 2×1 reconstruction of symmetric dimers with no buckling having a dimer-bond length of 1.36 Å similar to the isolated carbon double-bond length of 1.31 Å and in excellent agreement with other self-consistent results [19–21].

In conclusion, we have presented a self-consistent ab initio study on the atomic and electronic structure of the diamond (111) and (100) surface. The ground state of the C(111) 1D surface is the π -bonded chain structure and on the C(100) surface a symmetric-dimer structure. The energy gain on formation of both structures is due to strong σ -, π -double bonds in contrast to Si and Ge. The bond lengths are similar to the carbon double-bond length. The surface chains on the π -bonded chain model are found to be undimerized, in contrast to some other experimental and theoretical investigations. Two stable adatom-like structures are found to have an energy minimum at the C(111) 3D surface. The total energies at both minima are similar. The single-chain model forms π -chains giving rise to an electronic-band structure strongly resembling that of the π -bonded chain model but only in very weak agreement with the experimental data. The other structure is characterized by asymmetric trimers above H-site positions on the sublayer, the electronic structure possessing metallic character.

Summarizing the results for the electronic structure, one finds complete agreement for the C(100) surface. In the case of the C(111) $2 \times 2/2 \times 1$ surface more experimental and theoretical work is needed to give a clearer picture of the structure-related surface bands.

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