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Dimerized, buckled, or ideal chains on the diamond (111)2 × 1 surface?

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Abstract

We present fully converged ab initio density-functional calculations for the C(111)2 × 1 surface using soft carbon pseudopotentials and plane waves with a cutoff of 42 Ry. By means of a Car–Parrinello-like energy-minimization scheme π-bonded Pandey chains are found to form the ground state of the system. The surface-structural properties are studied in detail. Depending on the numerical details the π-bonded chains show a nearly vanishing dimerization and are unbuckled within the accuracy of our method. Consequences for the electronic structure are discussed.

Keywords: Density functional calculations; Diamond; Low index single crystal surfaces; Molecular dynamics; Surface relaxation and reconstruction

For both homoepitaxial and heteroepitaxial growth as for the fabrication of diamond–semiconductor or diamond–metal interfaces the thorough understanding of the low-index surfaces of diamond is of great importance. This holds especially for the C(111) face. Triple-dangling bond (glide plane) surfaces may occur on polycrystalline films deposited by chemical-vapour deposition besides single-dangling bond (shuffle plane) cleavage faces [1]. The LEED pattern of the clean latter one shows an apparent 2 × 2 translational symmetry but is commonly interpreted to arise from a superposition of three rotated 2 × 1 domains [2,3].

There is general agreement that a π-bonded chain model as introduced by Pandey [4] explains the reconstructed geometry of the C(111)2 × 1 surface. Experimental arguments are based on ion scattering [5], photoemission spectroscopy (PES) [6–8], and infrared–visible sum-frequency-generation (SFG) spectroscopy [9]. The support for the general nature of the reconstruction from theoretical studies [1,4,10–18] is accompanied by a controversial discussion of the precise structure, such as chain dimerization or chain buckling, and the origin of the surface gap of about 2 eV [19,20]. The solution of the puzzle is of both scientific and practical interest: (i) Jahn–Teller-like distortions, such as buckling, govern the chain reconstruction in the case of Si and Ge(111)2 × 1 surfaces. Multiple bonds, i.e. dimerization, are characteristic structural elements of aromatic carbon compounds. (ii) Are deviations from the ideal chain structure the only possible explanation for a surface gap opening along the JK line in the surface Brillouin zone (SBZ)? Total-energy calculations using both (semi)empirical [1,10,12–14,16] and

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ab initio [11,15,18] methods yielded contradicting results. Refs. [12,14,15,18] indicate that the surface π-bonded chains are dimerized. Undimerized (but sometimes slightly buckled) chains have been found to be energetically favourable in Refs. [10,11,13,16].

In this paper we present fully converged self-consistent total-energy and electronic structure calculations of the C(111)2×1 surface for the π-bonded chain model. Special care is given to the convergence of the calculations with respect to the number of plane waves applied, the size of the slab and the k-point sets used in the SBZ integration. To ensure to find the global minimum under the constraints of 2×1 translational symmetry at the single-dangling bond cleavage face, several modifications of the π-bonded chain geometry are taken as starting point of our total-energy minimization. Dimerization and buckling are studied in detail. The surface band structure computed for the minimum energy geometry is compared to the experimental findings and discussed with respect to the assumptions entering the calculational method.

Our calculations are based on the density-functional theory (DFT) and the local-density approximation (LDA) [21]. The electron–ion interaction is treated by norm-conserving, ab initio, fully separable pseudopotentials of the Bachelet–Hamann–Schluter type in the Kleinman–Bylander form. After softening the carbon pseudopotentials [22] the energy cutoff can be restricted to 42 Ry as shown in Fig. 1. This value is somewhat larger than the 34 Ry found to be sufficient for silicon carbide [22]. For bulk diamond the softened pseudopotential gives rise to a lattice constant of 3.534 Å, being 0.9% smaller than the experimental value (3.567 Å). The experimental values for the bulk modulus (4.42 Mbar) and the TO(Γ)-phonon frequency (250.7 THz) are with 4.56 Mbar and 245.1 THz, respectively, well reproduced. However, the DFT-LDA value for the indirect energy gap of 4.09 eV underestimates the experimental value (5.5 eV) by about 25%. In order to simulate the surfaces we use the repeated-slab method. Symmetric slabs of 12 atomic layers of carbon and a vacuum region equivalent in thickness are found to be sufficient to widely avoid splitting between the surface states at the top and the bottom of the slab as well as electrostatic interactions

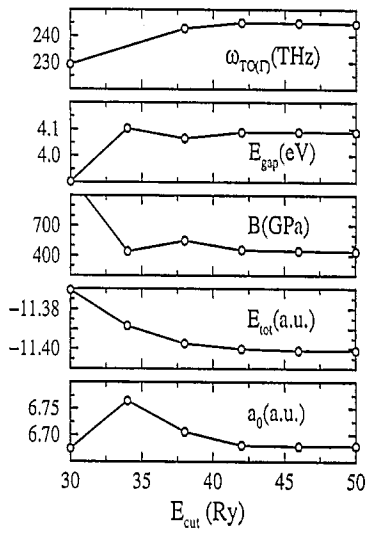

Fig. 1. Properties (TO(Γ) phonon frequency, gap energy, bulk modulus, total energy, and lattice constant) of bulk diamond versus the plane-wave cutoff E_{cut}.

through the vacuum region. The quality of the separation can be seen from the clear plateau in the electrostatic potential. The symmetry of the slab prevents any artificial dipole field, which may occur for instance upon attaching hydrogen to one side of the slab. The k-space integration is replaced by a summation over 16 special points in the full SBZ of the 2×1 surface. Since the resulting surface system is semimetallic we have checked the convergence applying denser k-point sets as described in detail below. To support the convergence we use a Fermi–Dirac occupation of states with a k_BT width of 0.01 eV. In order to determine the equilibrium positions, the atoms of the two innermost substrate layers are kept frozen whereas all other atoms are allowed to relax until the total energy and the forces on the atoms are minimized. No symmetry restrictions, e.g. the assumption of a mirror symmetry, are applied. We define convergence as reached when the atomic forces are smaller than 0.025 eV/Å. Simultaneously the single-particle wave functions are brought to self-consistency within a Car–Parrinello-like minimization scheme for the free-energy functional [21].

In order to find a global energy minimum we have tested a variety of 2×1 reconstruction models for the C(111) surface as starting geometries. In agreement with previous calculations we find the

lowest energy for the π-bonded chain model. The energy gain of 1.40 eV/surface atom with respect to bulk-terminated surface is much larger than for other structures as the relaxed bulk-terminated surface (0.57 eV/surface atom) or Chadi's π-bonded molecule model (0.73 eV/surface atom). In our calculations a graphitic-like surface reconstruction recently discussed as a metastable state [23] on the (111) face is found to give only a saddle point at the total-energy surface. It immediately transforms into the relaxed bulk-terminated surface. The energy gain observed for the optimized chain structure lies within the scale of other theoretical findings 0.82 [10], 0.68 [11], 0.70 [13], 1.85 [14], 1.08 [16], and 0.63 eV [18]. The geometrical details of the resulting π-bonded chain structure are consistent with results of other ab initio calculations [11,15,18] and several semiempirical calculations [10,12–14,16] as can be seen from Table 1. This holds especially for the averaged intrachain bond length d and the distance between the second and third atomic layer. The values of the chain bond length d are between the length of a single C–C bond (1.51 Å) and that of a double C=C bond (1.34 Å) and approach the in-plane bond length in graphite. This indicates the delocalized nature of the surface states related to the π-bonds. The bonds between the second and third atomic layer are remarkably lengthened. However, our values of 4.5 and 6.6% are somewhat smaller than those obtained within earlier ab initio calculations [11,15]. The reason may be related to the atomic relaxations in the fourth and fifth atomic layer allowed in our calculation. The corresponding bond lengths are shortened by 2.8% or lengthened by 4.3%, resulting in a substantial buckling in these layers beneath the surface. In agreement with Refs. [11,15] the bond lengths between the first and second layer, d_2 an d_2', and that within the second layer, d_3, (cf. Fig. 2) deviate only little from the bulk diamond bond length. The effect is larger for

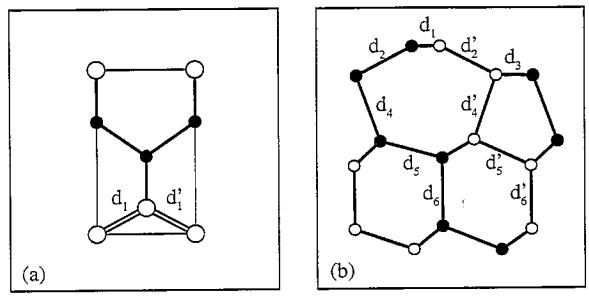

Fig. 2. Illustration of important bond lengths in the top (a) and side (b) view of the π-bonded chain model.

Table 1
Structural parameters (cf. Fig. 2) of the optimized π-bonded chain reconstruction of the C(111)2×1 surface

Method	d	Δ	b	d_2	d_2'	d_3	d_4	d_4'
Experimental								
LEED [3]	1.51	0.0		−3.6	−3.6		8.0	8.0
Semiempirical								
Tight-binding [10]	1.45	0.0	0.00					
MNDO-cluster [12]	1.45	5.0	0.02	0.8	−1.7	4.7	6.6	7.7
Tight-binding [13]	1.50	0.0	0.04					
SLAB-MINDO [14]	1.47	4.1	0.01	−2.0	−2.0	1.2	3.6	3.6
Tight-binding [16]	1.44 (1.48)	0.6 (0.2)					9.0 (6.0)	9.0 (6.0)
Ab initio								
Local orbitals [11]	1.47	0.0	0.04	0.7	0.7	0.7	8.1	8.1
Plane waves [15]	1.44	1.4	0.00	<2.0	<2.0	<2.0	8.0	8.0
Local orbitals [18]	1.44	?	0.00					
Present results	1.43 (1.44)	0.0 (0.3)	<0.01 (<0.01)	0.1 (0.0)	−0.1 (−0.2)	0.9 (0.8)	6.6 (6.8)	4.5 (4.6)

The chain bond lengths d_1 and d_1' are given by their average $d=(d_1+d_1')/2$ (in Å) and the degree of dimerization $\Delta=(d_1-d_1')/(d_1+d_1')$ (in %). The buckling b of the π-bonded chain is given in Å. The changes of the bond lengths d_2, d_2', d_3, d_4, and d_4' with respect to the ideal bulk value are given in %. In addition to our results calculated with 16 k-points in the full SBZ and a cutoff of 42 Ry, structural data obtained for 64 k-points and 34 Ry are given in parentheses. The different tight-binding results [16] concern 24 (12) atomic layers in the slab

the bonds between third and fourth atomic layer in the $(01\bar{1})$ plane.

The influence of the k-point sampling on the structural details of the π-bonded chain geometry has been extensively tested with finer k-point meshs as shown in Fig. 3. This figure shows special k-point sets of 4, 8 and 16 points in one quarter of the SBZ. Of particular interest is the 16 k-point set suggested by Vanderbilt and Louie [11], which is very dense along the JK line where the surface bands in the fundamental gap are nearly degenerated and cause the semimetallic behaviour of this surface (cf. discussion of Fig. 5). In order to perform the calculations with these 16 special points giving rise to altogether 64 k-points when folded into the full SBZ we had to reduce the plane-wave cutoff to 34 Ry. The resulting chain geometry for the Vanderbilt k-point set is given additionally in Table 1. We find that neither the increase of the number of k-points nor their inhomogeneous distribution give rise to remarkable changes. Even the increase of the density near the zone boundary does not essentially change the findings. The crucial difference in the results of the various calculations concerns the dimerization of the π-bonded chains. In our computations we find an almost vanishing dimerization, nearly independent of the computational details. Our total-energy calculations (cf. Fig. 4) show that the π-bonded chain structure is, in fact, stable against any significant dimerization in agreement with other calculations [10,11]. Small initial dimerizations were found to revert to symmetry upon force minimization. Indeed, an initial dimerization of a few percent vanishes rather quickly after few time steps of the Car–Parrinello-like minimization procedure. Much more steps are needed to restore the mirror symmetry on the surface, i.e., to reduce the displacement of the chain in $[01\bar{1}]$ direction against its ideal position. We observe a small variation of the almost vanishing dimerization in dependence on the numerical details. For a cutoff of 34 Ry and varying numbers of k-points in the SBZ we find $\Delta = 0.03\%$ (16 points), 0.18% (32 points), 0.18% (64 points) and 0.30% (64 points but inhomogeneously distributed according to Ref. [11]). Although tiny, there is a small influence of the k-point set on the degree of dimerization. The smallness of the dimerization and its k-point set dependence are in agreement with recent DFT-LDA calculations [24] and our own studies of *trans*-polyacetylene. Obviously the inhomogeneous k-point set causes, mediated via the band structure energy, a slight increase of the dimerization.

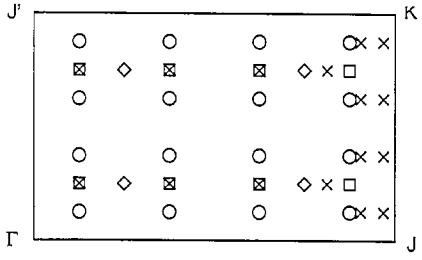

Fig. 3. k-point samplings within one quarter of the SBZ of the $(111)2 \times 1$ surface. This part is equivalent to the irreducible part of the SBZ of a p-rectangular lattice only in case of a 2 mm point-group symmetry of the surface. Our calculations were performe d using these points but folded into the full SBZ. Diamonds indicate four special points, squares: eight special points, circles: 16 special points and crosses denote 16 points, that are denser in the vicinity of the zone edge (according to Ref. [11]).

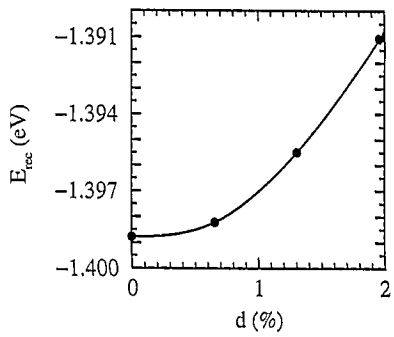

Fig. 4. Total energy (per surface atom and with respect to the ideal surface) versus dimerization obtained from a calculation with 16 special points in the full SBZ.

However, our results indicate by nearly a factor of five smaller dimerization than another ab initio DFT-LDA calculation [15] which ended up with $\Delta = 1.4\%$. Apart from deviations in the computational details, no clear explanation can be given. However, there are some arguments in favour of a very small symmetry break. Dimerization of the surface π-bonded chains can be interpreted as a Peierls-like transition analogous to that in *trans*-polyacetylene. It opens a remarkable energy gap in the chain band structure accompanied by a lowering of the total energy. However, this analogy

is only approximate since the bonds of chain carbon atoms to the diamond substrate do not behave as bonds to hydrogen atoms do. Therefore the dimerization of the surface chains is accompanied by two competitive tendencies in the total energy. The energy gain due to the lowering of the occupied surface band is counterbalanced by the energy costs of additional strain in the subsurface atomic layers. Thus, we expect a dimerization that is essentially smaller than the 1.6% [25] and 2% [26] measured for free finite polyacetylene chains. An additional argument for a smaller dimerization than observed for these free organic molecules is the assumed infinity of the π-bonded surface chains in our calculation.

Because of the observed stability against the formation of alternating single and double bonds Chadi [10] suggested the possibility of a much larger dimerization leading to the rupture of one bond and the formation of a triple bond. We have used the strongly dimerized structure of Chadi as the starting geometry of the Car–Parrinello procedure. The shortened bond is shrinked by 18% compared to the bulk diamond length, and the lengthened bond is stretched by 44%, effectively breaking it. In contrast to the tight-binding approach of Chadi [10] we did not find a local minimum for this structure on the Born–Oppenheimer total-energy face. The structure corresponds only to a saddle point. Our optimization ends up with an almost undimerized π-bonded chain surface.

A similar tendency as for the reversion of the initial dimerization is found for an initial buckling of the π-bonded chains. After the relaxation of the atomic coordinates we end up with buckling amplitudes <0.01 Å. Summarizing the results, we observe a tendency for symmetrization of the structure parallel to the chain direction. The arguments for vanishing buckling are simpler than for the vanishing dimerization. A chain buckling weakens the π-bonds and, hence, rises the total energy. The charge transfer between the chain atoms should be small due to the localized nature of the carbon orbitals. Consequently, the same holds for the accompanying energy gain. However, the polarization dependence of a nonlinear spectroscopy recently published [9] strongly supports buckled chains. This type of spectroscopy is sensitive to the bond orientation. The polarization anisotropy may only be explained by surface C–C bonds which have a component perpendicular to the surface.

The band structure of the C(111)2×1 surface in the region of the fundamental gap of the projected bulk band structure is shown in Fig. 5 for the almost undimerized π-bonded chain model optimized with 16 k-points. The dominating features are the π^*- and π-like surface bands, similar to the bands observed in many other calculations. The highly dispersive character of the bands in the ΓJ, and KJ′ regions as well as their flatness and near degeneracy along the JK line indicate their origin from bonding and antibonding combinations of chain p-orbitals parallel to the surface normal. At Γ the surface bands are nearly degenerated with bulk states. The splitting of unoccupied and occupied states of about 4.8 eV agrees with values 4.8 [11], 3.0 [15], and 5.0 eV [18] from other ab initio calculations. The seemingly good agreement with measurements of the two-photon PES [8] as well as the agreement with angle-resolved PES [6,7] for the upward dispersion of the occupied surface band along ΓJ is more fortuitous. In agreement with Vanderbilt and Louie [11] and Alfonso et al. [18] the surface bands become nearly degenerated at J. The bands slightly increase in JK direction (which is the direction perpendicular to the chains) and cross the Fermi level causing the semimetallic character of the surface. The small dispersion and splitting of the

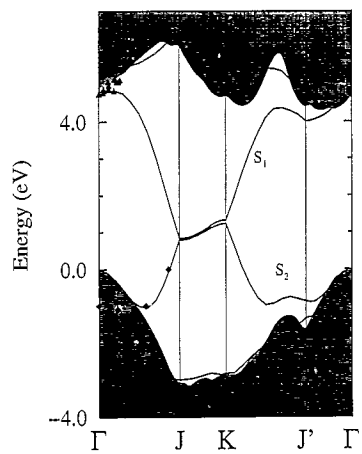

Fig. 5. Band structure of the C(111)2×1 surface for the optimized π-bonded chain structure.

bands along JK measure the interaction of the chains with the substrate as well as a weak interchain interaction. The introduction of the dimerization of about 1.4% makes the surface semiconducting. However, the gap opening at J remains small with 0.3 eV [15].

The consideration of the quasiparticle aspect should remarkably change the excitation energies. This is exactly described by Kress et al. [17] applying the GW approximation to the C(111)2 × 1 surface. Indeed strong shifts of the energies have been calculated at Γ. However, at J the gap opening by quasiparticle effects only amounts to 0.25 eV. This value is too small to explain the experimental surface gap of 1.0 eV or even 2.1 eV [19,20]. Therefore, Kress et al. started from a dimerized π-bonded chain structure and indeed found a significantly larger surface gap. They appreciated this result as support for the dimerized π-bonded chain model. In the light of the recent discussion the result for the undimerized chain is questionable since the standard perturbational treatment of the quasiparticle corrections was applied to (nearly) degenerated surface states. Instead, the full quasiparticle equations should be solved from the very beginning to get a definite answer.

In summary, we have performed DFT-LDA calculations for various atomic configurations of the C(111)2 × 1 surface. We found almost undimerized and unbuckled π-bonded chains the energetically most favourable structural elements. Graphitization and strong dimerization cannot occur at the free surface for energetic reasons. However, the DFT-LDA band structure belonging to the π-bonded chain structure cannot explain all experimental details concerning excitation energies and polarization dependencies. We hope to stimulate further (especially experimental) work in the field. This holds in particular for structural studies by dynamical LEED and other methods, but also for the investigation of the electronic states near the Brillouin zone boundary by means of angle-resolved photoemission, inverse photoemission, and EELS.

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