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Quasi-particle band structure of $C(111)2 \times 1$ and $C(100)2 \times 1$ surfaces

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Abstract

Quasi-particle band structure calculations are performed for the geometry-optimized diamond $(111)2 \times 1$ and $(100)2 \times 1$ surfaces within the GW approximation. The $C(111)2 \times 1$ surface exhibits a strong reconstruction resulting in π -bonded chains of surface atoms. However, the precise positions of the chain atoms are still under debate. Ideal, buckled, and dimerized chains are discussed. We find agreement with spectroscopic data, including the correct surface gap, only for the dimerized structure. From an ab initio total energy minimization within DFT-LDA we favour the 2×1 symmetric dimer reconstruction for the $C(100)$ surface. The resulting quasi-particle band structure exhibits two well separated (dangling-bond related) surface bands within the fundamental gap.

Keywords: Density functional calculations; Diamond; Low index single crystal surfaces; Many body and quasi-particle theories; Surface electronic phenomena; Surface relaxation and reconstruction

The diamond $(111)2 \times 1$ surface is technologically important and theoretically prototypical. It has been the subject of a remarkable number of both theoretical [1–3] and experimental [3–7] investigations. Agreement has been reached concerning the similarity of the reconstruction mechanism to that of the $Si(111)2 \times 1$ surface. The Pandey π -bonded chain model [8] is clearly favoured. However, the precise positions of the atoms in the unit cell are still under debate. A surface gap opening is discussed due to either a buckling [1] or a dimerization [2] of the chains.

Recently, the diamond (100) surface has attracted new interest due to the challenging technological advances of nearly atomically smooth thin-film growth of this surface by chemical vapour deposition

methods [9,10]. Meanwhile, there are also theoretical [3,11–13] and experimental [3,14,15] studies of the structural and electronic properties of this surface. However, the question of both the particular geometry and the cleanness of this surface is open. By analogy to $Si(100)$ [16] symmetric and asymmetric dimer reconstructions are discussed.

Theoretical state-of-the-art investigations of the electronic properties [1] and/or the atomic geometry [1,17] of surfaces start from the density-functional theory (DFT) in local density approximation (LDA). However, concerning the electronic band structure there is a serious lack in these calculations related to the identification of the single-particle Kohn–Sham (KS) eigenvalues $\epsilon_{\nu}^{KS}(\mathbf{k})$ (ν the band index, $\mathbf{k}$ the wave vector from the surface Brillouin zone (SBZ)) with excitation energies [18]. Energy gaps are system-

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atically underestimated and the placement of occupied surface-state energies is commonly too high, relative to the bulk valence bands. This problem can be solved by treating the excitations within the quasi-particle (QP) Green's function formalism and calculating the exchange correlation (XC) self-energy linear in the screened Coulomb potential, i.e. within Hedin's GW approximation [18]. In this limit the energy $\varepsilon_\nu(\mathbf{k})$ of the quasi-particle, more strictly speaking the position of the main peak in the spectral function belonging to G , is shifted by $\Delta_\nu(\mathbf{k}) = \varepsilon_\nu(\mathbf{k}) - \varepsilon_\nu^{\text{KS}}(\mathbf{k})$ with respect to the corresponding KS eigenvalue.

The calculations of the QP shifts constitute a rather complicated problem, especially for surfaces [16,18]. However, restricting to the main effect in bulk materials due to the static and diagonal screening, the surface QP shift can be approximately described by [19,20]

$$\begin{aligned} \Delta_\nu(\mathbf{k}) = & \frac{1}{2F} \sum_{\mathbf{q}} \sum_{\mathbf{G}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dz dz' \\ & \times [W(\mathbf{q} + \mathbf{G}, z, z') - W^h(\mathbf{q} + \mathbf{G}, z, z')] \\ & \times \sum_{\mathbf{k}'} \sum_{\nu'} B_{\nu\nu'}^{kk'}(\mathbf{q} + \mathbf{G}, z') B_{\nu\nu'}^{kk'}(\mathbf{q} + \mathbf{G}, z) \\ & \times \text{sign}(\varepsilon_{\nu'}(\mathbf{k}') - \mu), \end{aligned} \quad (1)$$

with 2D Bloch integrals $B_{\nu\nu'}^{kk'}(\mathbf{q} + \mathbf{G}, z)$ and 2D wave vectors $\mathbf{q}, \mathbf{k}, \mathbf{k}'$ from the SBZ. $\mathbf{G}$ is a 2D reciprocal lattice vector defined for a 2D crystal area F . The real space vector $\mathbf{x}$ is split into components, which are parallel and perpendicular to the surface, $\mathbf{x}_{\parallel}$ and z . μ denotes the chemical potential. W stands for the statically screened Coulomb potential of the truncated semiconductor, while W^h is that of the homogeneous electron gas. W^h occurs due to the replacement of the XC potential of the DFT-LDA [21].

In the sense of a first-order perturbation theory, the single-particle DFT-LDA eigenfunctions and eigenvalues entering expression (1) are calculated by means of a first-principles, self-consistent LCAO version of Vanderbilt and Louie [1]. This method relies on the variational principle for the treatment of intra-atomic charge transfer, but incorporates a fully self-consistent treatment of interatomic charge transfers. All wave functions and potentials are represented in terms of Gaussians on the site centers. Three decay constants are used for each s- or p-type Gaussian

orbital in the basis. The resulting QP corrections are rather independent of the underlying DFT-LDA calculation. In the C(100) case we take advantage of this fact and add the resulting QP shifts to the Kohn–Sham eigenvalues of another DFT-LDA version [17] in which the wave functions are expanded in plane waves and the electron–ion interaction is treated by using norm-conserving, *ab initio*, fully separable pseudopotentials. C pseudopotentials are softened so that an energy cutoff equal to 34 Ry is sufficient [22]. This version has the advantage that, simultaneously with the self-consistent calculations of the electronic structure, the atomic geometry can also be optimized within a Car–Parrinello-like minimization scheme of the total energy. We use the repeated slab method to simulate the surfaces. For instance, in the (100) case a single slab contains 12 (100) layers of carbon atoms and a vacuum region equivalent in thickness to 12 such layers.

In the case of the C(111) 2×1 surface we consider three different π -bonded chain structures [8], a nearly ideal (more strictly slightly buckled but undimerized) geometry [1], remarkably buckled chains where their buckling amplitude is taken from Si(111) 2×1 [23] but is downscaled, and also a dimerized chain structure [2]. As a typical example for the DFT-LDA band structures that result for dimerized chains is plotted in Fig. 1a. The most pronounced features within the fundamental gap, the two strongly dispersive surface bands, are rather independent of the specific surface geometry. Only the degree of the gap opening along the JK line varies somewhat with the structure. However, the dimerized chains give rise to an upper limit whereas the two other geometries show a semi-metallic character. The DFT-LDA result can be explained in terms of the interaction of p_z orbitals ($z \parallel [111]$) of neighbouring chain atoms at the positions τ_1 and τ_2 with the orbital energy ε_p and the interaction matrix element $V_{pp\pi}$ in a much clearer way than it is the case with silicon. For isolated chains a π^* - and a π -like surface band follows with

$$\begin{aligned} \varepsilon_{\pi^*/\pi}(\mathbf{k}) &= \varepsilon_p \pm |V_{pp\pi}| S(\mathbf{k}), \\ S(\mathbf{k}) &= \frac{1}{2} \sum_{i=1}^2 e^{i\mathbf{k}\tau_i}. \end{aligned} \quad (2)$$

For ideal or buckled chains the structure factor $S(\mathbf{k})$ vanishes at the JK boundary of the SBZ. Only a dimerization gives rise to a finite $S(\mathbf{k})$ resulting in the small

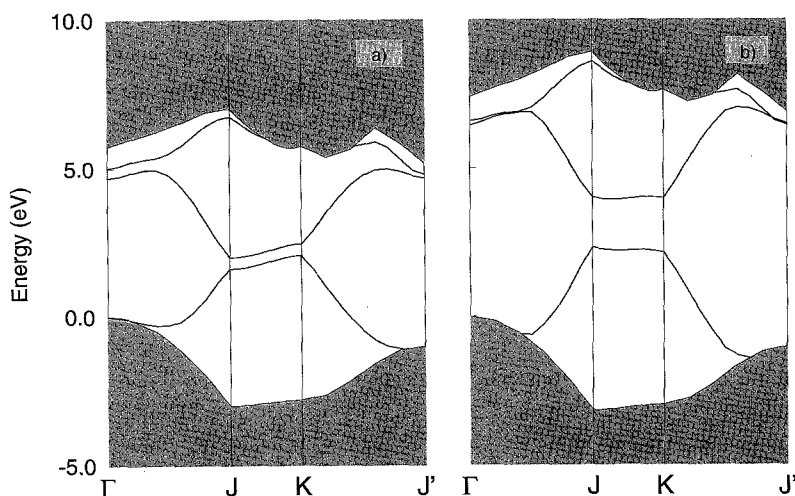


Fig. 1. DFT-LDA (a) and quasi-particle (b) band structures of the C(111) 2×1 surface for a dimerized π -bonded chain geometry [2]. The shaded region represents the projected bulk band structure. The VBM has been chosen to be the energy zero point.

gap along JK as shown in Fig. 1a.

The QP bands $\epsilon_p(k)$ have been calculated for the three geometries mentioned above. We find reasonable agreement of the QP band structure with experimental data only for the dimerized chains. The QP surface bands for this geometry are plotted in Fig. 1b together with the projected bulk band structure shifted by QP effects. We found that the QP corrections give rise to an upward shift of the π^* - and a downward shift for the π -bands along JK. According to the structure factor (2) already a small change of the chain structure due to the dimerization gives rise to remarkable QP gap corrections. The vanishing indirect surface DFT-LDA gap K $\rightarrow$ J is opened. The resulting direct gap at J of about 1.7 eV is reasonable, compared to the experimental findings of about 2 eV [4]. Due to the dispersion of the shifts the slope of the surface bands is reversed between J and K. The occupied π -like surface band becomes resonant near Γ . It lies about 1 eV below the valence-band maximum (VBM). The energetic position above the VBM of the π^* -like band near Γ is overestimated in comparison with the value of 4.8 eV measured by angle-resolved two-photon spectroscopy [7]. This discrepancy probably arises from the particular DFT-LDA band structure [1]. In this LCAO version the π^* -states lie already too high without QP corrections. The opening of the surface energy gap is finally a consequence of the chemical in-

equivalence of the chain atoms. The dimerization represents a Peierls-like distortion resulting always in a gap opening for free chains. For diamond the concept of weakly bound quasi-one-dimensional chains seems to be applicable. In the Si(111) 2×1 case the interaction of the chains with the substrate seems to be much stronger so that the dimerization is unfavourable and total-energy minimization [23] find a strong buckling.

In order to obtain reliable atomic geometries in the C(100) case we perform the first fully self-consistent *ab initio* pseudopotential calculations. The total energy is minimized for several atomic arrangements. These are symmetric and asymmetric dimer 2×1 reconstructions as well as a 2×2 surface reconstruction containing two oppositely buckled dimers. All these starting configurations relax to the same 2×1 reconstructed surface which is characterized by a symmetrically dimerized geometry in the top layer. This finding is in contrast to the *ab initio* DFT-LDA results for the Si(100) 2×1 surface [16,24,25], which have indicated a dimer buckling with a tilt angle of 14...17°. A possible reason is the tendency of the carbon atoms to form double bonds even at the surface. The energy gain due to the formation of a C=C double bond instead of a single bond as in the silicon case is larger than that due to the electron transfer between chemically inequivalent dimer atoms. Our optimized structure is similar to that resulting from a SLAB-MINDO

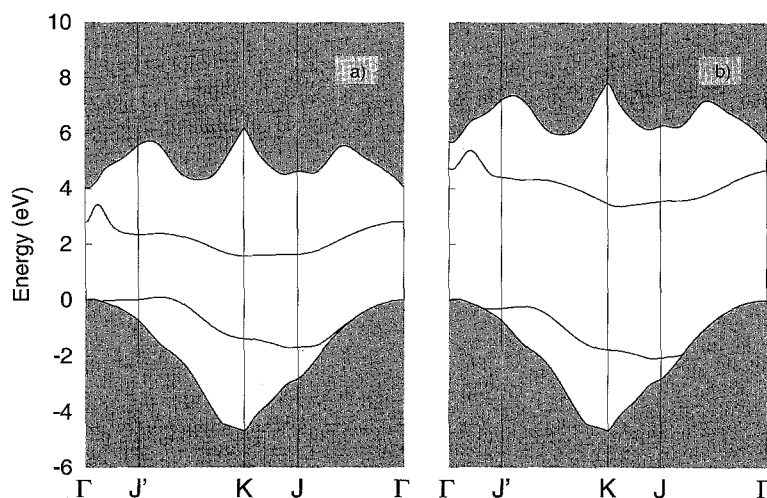


Fig. 2. DFT-LDA (a) and quasi-particle (b) band structures of the reconstructed C(100) 2×1 surface.

calculation [12]. The bond length of the carbon dimer is with 1.37 Å only slightly larger than the length of a C=C double bond of about 1.31 Å but remarkably smaller than a C–C single bond length of 1.58 Å. Other empirical and semiempirical studies [3,13] find a weaker dimer bonding and therefore a larger bond length. An interesting result of our calculations is the small asymmetry in the subsurface layers. It results in buckling amplitudes of 0.26 (0.14) Å in the third (fourth) atomic layer. That means, the formation of nearly doubly bonded surface dimers is accompanied by remarkable stresses in the subsurface layers. A further indication for this fact is the energy gain of 3.52 eV per 2×1 surface unit cell, which is much smaller than the formation energy of about 7.6 eV of a C=C double bond.

The electronic structures of the reconstructed C(100) 2×1 surface resulting within the DFT-LDA and the QP approach are represented in Fig. 2. They are qualitatively similar to band structures calculated for the Si(100) 2×1 surface [16,24,25]. The 2×1 reconstructed C(100) surface stabilized by strongly σ - and π -bonded dimers gives rise to two well separated bands of surface states within the SBZ. Despite the additional π -bonding, the two bands appearing in the fundamental gap are related to dangling bonds pointing nearly parallel to the surface normal. However, there are at least three differences to the findings in the Si case: (i) The lower (upper) surface band within

the gap is mainly built up by bonding (π (antibonding π^*)) combinations of the dangling orbitals and not by single dangling bonds located at the raised (lowered) dimer atoms. (ii) There is a remarkable energy gap between occupied and unoccupied surface states already without QP corrections. (iii) The surface bands exhibit a smaller dispersion over the whole SBZ.

The QP corrections shift the occupied DFT-LDA surface band down to lower energies (by -0.79 eV near Γ , by -0.88 eV at K) and the unoccupied surface band towards higher energies (by 1.47 eV at Γ , by 1.25 eV at K). The surface band gap is therefore opened in Fig. 2b by 2.14...2.35 eV throughout the SBZ. In contrast to the C(111) 2×1 case the QP correction of the gap varies rather weakly with k , in accordance with the small dispersion of the associated DFT-LDA bands. With QP corrections the occupied surface band is resonant with the bulk valence bands. Its maximum at $0.2 J/K$ is however only somewhat lower in energy than the VBM. The unoccupied surface band starting at 4.75 eV above VBM at Γ has a minimum near K of 3.3 eV above VBM which results in a band width of 1.45 eV, disregarding the hump near Γ . The gap between the surface states is indirect. The energy of the corresponding transition $0.2J/K \rightarrow K$ is nearly 3.7 eV.

In summary, we have performed QP calculations of various atomic configurations for the atoms in the π -bonded chains of the C(111) 2×1 surface as well as

for an energy-optimized geometry of the $C(100)2 \times 1$ face. In addition, in the $C(100)$ case the atomic geometry is optimized within the first fully self-consistent ab initio calculation for this surface. Both diamond surfaces exhibit two pronounced π^* - and π -like surface bands in the fundamental gap. However, a remarkable gap between these states for $C(111)2 \times 1$ can only be observed when starting from a considerable dimerization of the surface chains. In the $C(100)2 \times 1$ case the DFT-LDA gap is simply widened due to the QP effects. Thereby, the occupied π -like surface band becomes resonant with bulk valence states.

Acknowledgements

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