Electronic structure of the C(111) surface: Solution by self-consistent many-body calculations

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We present a first-principles calculation of the geometry and of the electronic structure for the C(111)(2 $\times$ 1) surface. We find that this surface reconstructs with π-bonded chains without any significant dimerization or buckling. At the DFT level, it appears semimetallic, in agreement with previous calculations, but in contrast to experimental evidence. Even the introduction of quasi-particle corrections within the usual *GW* scheme does not lead to the opening of the gap between surface states. Quasiparticle corrections to the surface band structure are hence calculated within a self-consistent *GW* scheme. A gap of about 1 eV is found between the surface states, thus finally solving the discrepancy between theory and experiment.

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The (111) face is the cleavage surface of diamond. Understanding its behavior is important from a technological point of view, the (111) plane is one of the growth surfaces for the chemical vapor deposition (CVD) of diamond, and from a theoretical point of view, in order to elucidate the principles of surface reconstructions in the other group IV semiconductors. Many potential applications of diamond arise from specific properties of its surfaces: while its negative electron affinity and unique surface conductivity make it attractive for electronic and optoelectronic devices,[1] its extreme surface chemical inertness makes it a good candidate for biomedical applications (reducing the chances of rejection); moreover, boron-doped diamond electrodes have been used in water purification and in the detection of many substances, especially biomolecules.[2] The exploitation of these potentialities relies strongly on the control and on the understanding of the chemical and physical properties of these surfaces.

Up to now no *ab initio* calculation was able to even qualitatively state if the clean cleavage surface of diamond was semiconducting or semimetallic. In this work we solve this problem and predict a surface state gap of 0.9 eV.

The geometry of the reconstructed C(111)(2 $\times$ 1) surface and the electronic band structure that originates from it are, in fact, still under debate. It is now well accepted that the reconstruction geometry of this surface is the Pandey π-chain model;[3] but the details of the relaxation, such as the presence of intrachain dimerization, buckling of the surface atoms, and deeper layer distortions, are still under debate. The exact determination of these details is important because, at the density functional theory (DFT[4]) level, the existence and the magnitude of the gap between surface states depend on them[5] in such a way that it is still not clear whether the semiconducting character of this surface is due to some geometrical deviations from the ideal Pandey chain model, or to other kind of symmetry breaking, i.e., antiferromagnetic spin ordering or, instead, to quasiparticle effects.

On the experimental side these geometrical details are not fully determined: x-ray diffraction structure analysis,[6] infrared-visible sum frequency generation measurements,[7] and ion scattering[8] find best agreement for an atomic arrangement featuring tilted chains, but can not completely rule out an unbuckled undimerized geometry. At the same time, core level binding-energy[9] and low-energy electron diffraction (LEED)[10] measurements see no evidence for buckling. Angle-resolved photoemission spectra,[11] while showing a strongly dispersing surface state that reaches its maximum 0.5 eV below the Fermi level, hence leading to a gap of at least 0.5 eV in the surface electronic structure, suggest that a dimerization of the chains has to be excluded for symmetry reasons.

So far, converged total energy calculations were not able to give a picture that completely agrees with the experimental results. All *ab initio* calculations[12–14] do not indicate either a chain buckling or a chain dimerization. Within the DFT-LDA[4] scheme, in the absence of dimerization, this surface appears metallic while, as already mentioned, experimental data show that its electronic structure has a gap of at least 0.5 eV;[11] electron energy loss spectra[15] suggest a gap that ranges from 1 eV (the onset of the loss feature) to 2.1 eV (the position of the peak).

Quasiparticle corrections to the surface band structure have been calculated within an approximate GW scheme[16] for several atomic configurations of the surface atoms. It was found that only a dimerized or strongly (nonphysically) buckled geometry could lead to an opening of the gap while neither a nearly ideal Pandey chain geometry nor a slightly buckled chain could do. The reason of the mismatch between the lowest-energy configuration and the configuration that seems to provide a better agreement for the electronic structure was thought to be possibly due[13] to the fact that the quasiparticle corrections had been calculated within a first-order perturbative approach, starting from DFT energies.

The situation thus calls for new and more refined calculations. It is, in fact, hardly believable that the cleavage surface of a wide gap semiconductor, as diamond, is metallic. There are two possible reasons for the fact that within DFT this surface results to be metallic: either the geometry found within DFT-LDA is wrong, or the band structure, calculated within DFT-LDA and approximate *GW* schemes, is wrong. As a first step, hence, we performed a new DFT calculation for the equilibrium geometry,[17] going beyond the usual LDA scheme, utilizing a GGA exchange correlation potential.[19] As a second step, we have calculated the electronic band struc-

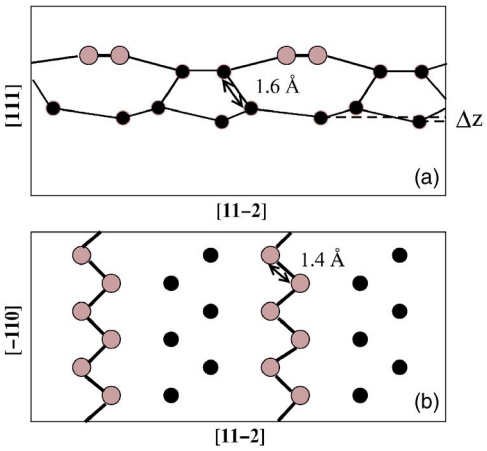

FIG. 1. (Color online) Geometric structure of the surface. (a) Side view. (b) Top view. The atoms belonging to the top chains are gray; the relaxed structure is unbuckled and undimerized. On the fourth layer a relatively strong buckling Δz=0.17 Å is present.

ture within the many-body Green's function approach using a self-consistent scheme. We find that the latter approach yields a sizable gap between surface states and an electronic structure, in agreement with photoemission experiments.

In the optimization of the geometry we started from several configurations, involving Pandey chains with slight negative and positive buckling[20] and dimerization. The final relaxed geometry, common to all the starting points, is shown in Fig. 1. We find that the buckling and the dimerization of the chains vanish, thus confirming previous DFT-LDA results.[13,14]

Having confirmed the state-of-the-art equilibrium geometry for C(111)(2×1), the next point to clarify is the electronic band structure. The resulting DFT-GGA electronic band structure is shown in Fig. 2. The surface bands that lie in the gap are originated by the bonding and antibonding combinations of the π orbitals of the atoms in the chains. As shown in Fig. 1(b), the chains develop in the $[\bar{1}10]$ direction and are an almost one-dimensional structure; this characteristic should lead to a strong dispersion of the surface bands along the chain direction that correspond to the ΓJ and KJ' parts of the IBZ boundaries and, *vice versa*, to a less dispersive behavior along the directions perpendicular to the

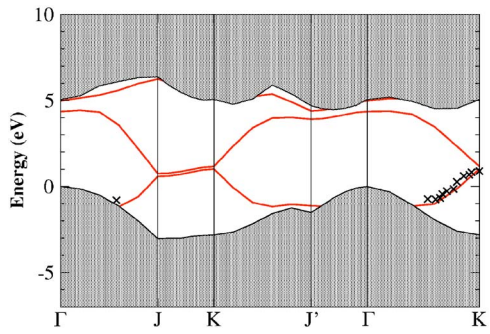

FIG. 2. (Color online) DFT-GGA electronic band structure of the C(111)(2×1) surface. Crosses: experimental data from angle-resolved PES from Ref. 21 and from Ref. 11.

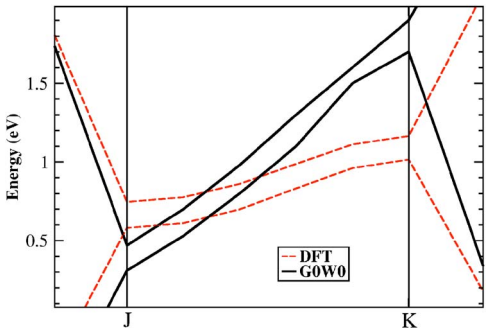

FIG. 3. (Color online) Surface states within the DFT-GGA (dashed lines) and within the G_0W_0 scheme (solid lines).

chains, which correspond to the JK and $J'\Gamma$ directions. The calculated band structure shown in Fig. 2 is in good agreement with these expectations, and the dispersion of the calculated bands is in qualitatively good agreement with experimental data points. However, in the JK directions the calculated two surface bands are nearly degenerate and their upward dispersion (~0.4 eV) makes them cross the Fermi level producing a semimetallic surface. This is in contrast with experimental data that predict a gap of at least 0.5 eV.[11] An opening of the gap could happen in the presence of a dimerized chain, which we do not find, nor does it seem suggested by experiments. Also a test calculation[22] performed within LSDA[23] did not change this picture because the system relaxed to a nonmagnetic configuration.

DFT (within LDA or GGA schemes) is known to underestimate the gap of semiconductors. DFT itself, in fact, is an exact theory when applied to ground state properties but, in principle, there is no formal justification to the use of this theory for excited state properties. The absence of the gap between surface states at the C(111)(2×1) surface may be due to this reason.

Hence, we have calculated quasiparticle corrections to the DFT energies, by evaluating the diagonal elements of $(\Sigma - V_{xc}^{DFT})$[27] between DFT states, using for the self-energy $\Sigma = iG_0W_0$.[24–26] G_0 is the single-particle Green's function and W_0 the screened Coulomb interaction. The subscript 0 refers to the fact that both G and W are calculated using DFT wave functions and eigenvalues. The results are shown in Fig. 3.

As is clear from the figure, the G_0W_0 corrections do not change the situation: the upward dispersion from J to K of the nearly degenerate bands, which caused the metallicity of the surface, is still present. This is due to the fact that at the DFT level the two surface states at J are lower in energy than the two surface states at K. As a consequence of such energy band ordering, the states at J result occupied and those at K empty. GW corrections, which strongly depend on the occupancy of the states, cannot open a gap in this case since the starting DFT band structure has a wrong occupation of the bands. Hence, for this system, the usual G_0W_0 scheme does not work, and we have to go to more refined schemes.

A test calculation within the nonperturbative GW scheme described in Ref. 28, including the off-diagonal elements of Σ, also did not give any improvement to the band gap, since the off-diagonal elements are very small (two orders of magnitude smaller than the diagonal ones). In other words, the

quasiparticle wave functions are well represented by the DFT one. This is a consequence of the different symmetry of the Bloch sums at J built with the dangling bonds of the two surface atoms in the (2×1) cell: one is even under reflection with respect to the $(1\bar{1}0)$ plane, while the other one is odd. Hence they cannot be mixed by the Hamiltonian. In a two-dimensional model, this is true all along the JK line; hence no gap opening can be generated by a mixing of DFT wave functions of dangling-bond-like surface states.

Of course, in principle, the exact single-particle excitation energies can be obtained, solving the quasiparticle equation self-consistently within the Hedin equations,[24] but this procedure cannot be performed numerically for realistic systems. In the presence of a correct band ordering already at the DFT-GGA level, the solution is known and represents the state-of-the-art method for computing a band structure: one has to expand the quasiparticle wave functions in terms of the Kohn-Sham GGA orbitals and first-order perturbation theory is sufficient to compute quasiparticle energies. Here we have, within DFT-GGA or LDA, a wrong band ordering with respect to the energy; hence we have to search for a new procedure. There are two possibilities: either we slightly modify the exchange correlation potential from the beginning (during the DFT calculation) in order to open the gap and then use the well-known procedure based on the calculation of the quasiparticle states within first-order perturbation theory; or we use the eigenvalues and eigenfunctions of the Kohn-Sham problem, but start with the correct occupation of the states with a certain symmetry. We have tested the first possibility by using a Slater exchange potential, but the surface stays semimetallic, thus not providing a better starting point for the GW computation. Hence, following the second possible scheme, we have carried out GW calculations using Kohn-Sham eigenvalues and eigenfunctions, starting from an artificial electronic configuration in which the states with the correct symmetry were occupied. This approach finds a justification only if a self-consistent scheme is subsequently applied, and if the converged result does not depend on the starting point. In this spirit, we have performed a GW calculation, updating the quasiparticle energies until self-consistency was obtained. While reaching self-consistency, we could choose to update the eigenvalues only for the Green's function part of Σ, or for both the Green's function and the screening part, which, of course, is a much more time-consuming procedure. At each step, the updating of the eigenvalues was performed using the GW corrections from the previous calculation. A test with a 5 $\vec{k}$ point mesh showed that the converged values of the gap was reached already at the first iteration within 0.1 eV. The changes at the subsequent steps of the calculation turned out to be very small for both the updated and nonupdated screening procedure. Taking this result into account, we performed a much more elaborated calculation using 13 $\vec{k}$ points mesh in the IBZ. The results are listed in Table I: a minimum gap of about 1 eV opens between the surface states at J. Both procedures (updating only G, or updating G and W) lead to a semiconducting surface, and a good agreement with the available photoemission experiments is found (Fig. 4). As a final test we have performed, for the 5 $\vec{k}$ points mesh, the GW calculation starting from an arbitrarily large (1.6 eV) and small (0.6 eV) gap between J and K. Already at the first step of the computation of the quasiparticle energies, we found a value of the gap within 0.1 eV from the converged one for the nonupdated screening procedure and within 0.2 eV for the updated screening procedure, making sure in this way that the final converged value is independent of the starting point.[29]

TABLE I. The gaps between surface states within DFT and for each GW self-consistency cycle. The subscripts of the GW gaps refer to the iteration number: G_0W_0, G_1W_0, G_1W_1 values of the gap are related, respectively, to the GW calculation obtained directly using the DFT eigenvalues, updating the eigenvalues only in G, and updating the eigenvalues both in G, and in W. All energies are expressed in eV.

Gap	J	K	Γ	J'
DFT	0.16	0.15	4.52	5.03
G_0W_0	0.19	0.18	6.07	6.30
G_1W_0	1.06	1.06	5.82	6.27
G_1W_1	0.93	0.95	5.71	6.17

The issue of self-consistency within GW is still very controversial: there are many possible levels of self consistency (i.e., updating also the wave functions, including the quasiparticle renormalization factor or not, etc.) and the different methods yield different results depending also on the implementation of an all-electron or a pseudopotential scheme.[30] The simple update of the quasiparticle energies has already been implemented in previous calculations by other groups. In systems with semimetallic band structures at the LDA level,[31] and in systems for which G_0W_0 does not give good agreement with experiments,[32] the update of the quasiparticle energies yields improved results. This latter approach has also been substantiated by a recent study of vertex corrections within self-consistent GW: vertex corrections in W and in the self-energy cancel each other to a good extent, while the energy update yields relevant changes of quasiparticle energies.[33] Also in our calculations, carried out according to this procedure, the self-consistent scheme leads to a better agreement with experiments.

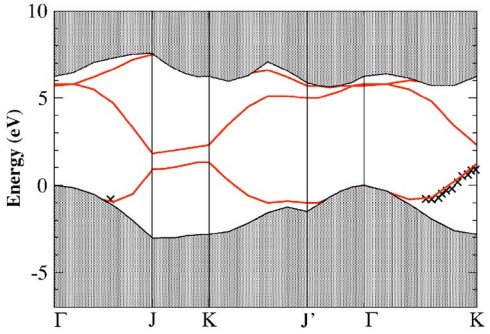

FIG. 4. (Color online) Electronic band structure of the C(111)2×1 surface within the self-consistent GW scheme. A gap of about 1 eV opens along the JK direction. Crosses: experimental results from Refs. 11 and 21.

In conclusion, we have solved the puzzle concerning the electronic structure of the diamond (111) (2×1) surface; its insulating character is not a consequence of asymmetric geometrical changes, rather of many-body effects. Using a self-consistent quasiparticle approach we have found a surface-state gap of about 1 eV (Fig. 4). This value is independent from the starting configuration, being it either an artificial *ad hoc* occupied configuration, or a configuration in which the conduction band was shifted rigidly by a small or big amount; it is compatible with the experimental findings ranging from 0.5 to 2.0 eV, and it reconciles experiment and theory for this surface. The energies of filled surface states are in good agreement with photoemission data. To our knowledge this the first *ab initio* calculation that yields a nonvanishing gap between the surface states of the C(111) $\times(2\times1)$ surface. We believe that the present work will foster new experimental works, e.g., optical absorption and/or EEL experiments to confirm our findings.

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