

Comment on “Diamond (111) surface reconstruction and epitaxial graphene interface”

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(Received 17 July 2023; accepted 8 January 2025; published 20 March 2025)

In a recent paper by Reed *et al.* [Phys. Rev. B **105**, 205304 (2022)], angle resolved photoemission spectroscopy (ARPES) experimental results as well as density functional theory (DFT) calculations performed on the diamond C(111)-(2 × 1) surface, both clean and graphene covered, are presented. We only address the first part of the paper (clean surface). On the basis of their photoemission data, the authors claim that the C(111)-(2 × 1) surface is metallic, adding that “our ARPES measurements do not compare well” with previous experimental results. Indeed, in the literature one can find a number of results obtained with different techniques, including ARPES, proving the semiconducting character of this surface. In this Comment we disagree with the interpretation of the experimental data given in the paper and conclude that the surface is semiconducting and any disagreement with published results is almost completely eliminated. We also discuss the theoretical approach used, placing it in a wider framework. When well founded, also the theoretical simulation shows the semiconducting character of the C(111)-(2 × 1) surface.

DOI: [10.1103/PhysRevB.111.117301](https://doi.org/10.1103/PhysRevB.111.117301)

The authors of Ref. [1] kindly provided the experimental data used in Figs. 1 and 2.

I. EXPERIMENTAL PART

In Ref. [1], the C(111)-(2 × 1) surface is claimed to be metallic since “it has electronic states that intersect the Fermi level” (Abstract) and it has “a metallic surface state that intersects E_f at the K point” (Conclusions). The K point is the top of the occupied surface state band. These statements are based mainly on the ARPES data shown in Figs. 2(e) and 2(f) of the paper.

A different interpretation of the experimental results allows us to conclude that the C(111)-(2 × 1) surface is semiconducting instead of metallic. We focus our discussion on two issues: the position of the K point with respect to E_f [Fig. 2(e)] and the shape of the leading edge in the energy distribution curve (EDC) at K [Fig. 2(f)].

In the left panel of Fig. 2(e) of Ref. [1], the output of a theoretical calculation is superimposed to the experimental ARPES results. While the result of the calculation is represented by a narrow line, experimental data points are arranged in a stripe (see the region between the K point and midway along the K - Γ direction). Near the K point the stripe bends to a maximum close to E_f , as can be better seen below in the enlargement of Fig. 1. The stripe is at least 0.6 eV broad (this value is ill-defined, of course) and its mean value lies some 0.25 eV below E_f , while its upper edge reaches E_f . Obviously,

the binding energy of K corresponds to the center (or mean value) of the stripe, not to the upper edge. Therefore we do not agree that the K point and E_f are coincident, as stated in Ref. [1], and the diamond C(111)-(2 × 1) surface appears to be semiconducting.¹

The high quality of the sample and the performance of the experimental setup offer the possibility to appreciate a more accurate value than in the past [3] for the so-called photoemission gap, which turns out to be about 0.25 eV. The semiconducting character of this surface was already established with different techniques a long time ago [2–4] and confirmed more recently [5]. The last (optical) measurements yielded a value of 1.5 eV for the gap, which undergoes a blueshift after exposure to contaminants. These results are in perfect agreement with those acquired on the semiconducting Si(111)-(2 × 1) and Ge(111)-(2 × 1) surfaces [5–7], suggesting a common interpretation for the (111) reconstructed surface of the IV group. In general, ARPES measurements are not expected to yield information about the energy gap, for the obvious reason that empty states are not probed. However, this is not totally true in the present case. If the surface band picture were as depicted in Fig. 1(d), with zero gap and the K point above the Fermi level,² then there should not be any photoemission of electrons from the K point. The fact that,

¹Even “degenerate semiconductor” would not be an appropriate definition in this case.

²The upward dispersion of the surface bands in diamond C(111)-(2 × 1), from J to K , is a feature present in all available calculations.

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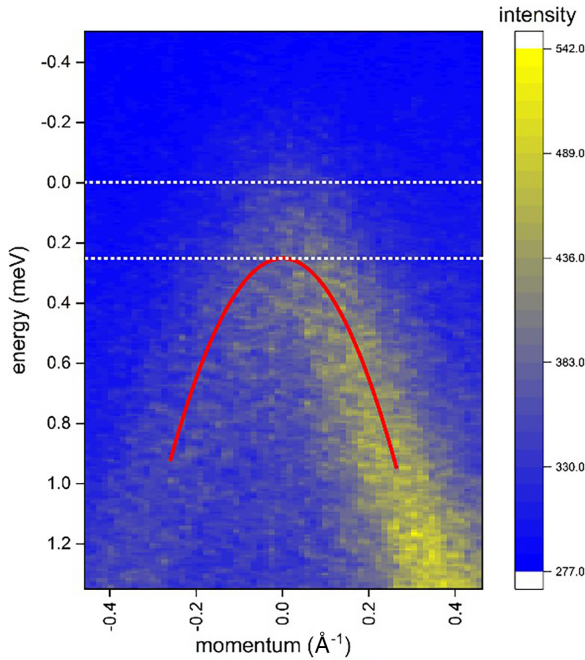


FIG. 1. Blowup of the ARPES data of Fig. 2(e) [1] near the K point. The 0- and 0.25-eV binding energies are highlighted (white dotted lines). An inverted parabola approximately through the center of the stripe is also shown, as a guide for the eye.

instead, the K point is fully visible (see Fig. 1) agrees with the existence of an energy gap, whereby K is pushed below E_f .

We now consider Fig. 2(f) of Ref. [1], showing an EDC at the K point, integrated over k values comprised in a small range near the K point [between the two white dashed lines shown in Fig. 2(e)]. According to the interpretation given in Ref. [1], “...the EDC taken at K shows that the state is indeed metallic as its leading edge is best fitted with a Fermi function at 0 eV and a width representative of a sample temperature of 300 K.” Indeed, the best fit is drawn in Fig. 2(f) as a blue line, which can be better seen by magnifying the figure. We disagree with this interpretation because the blue line, or leading edge, is by far too broad to be identified with a Fermi edge at room temperature (whose width is about $4\text{ kT} = 100\text{ meV}$) even by adding the instrumental resolution, which is also 100 meV [8]. In our opinion no Fermi edge is visible in this spectrum, while the peak just below E_f is associated with the K point, i.e., with the center of the stripe of Fig. 1, as stated above.³

The width of this peak is similar to the width of photoemission from the Γ point (see the magenta curve in Fig. 2(g) of Ref. [1]), which is described as follows: “...the FWHM of the π band [surfacelike] is almost double that of the σ band [bulklike]. An increase in the FWHM like this could result from an increased density of defects present within the Pandey chains. These defects most likely result from polishing lines or

³Incidentally, in the Supplemental Material of Ref. [1], Fig. S2, the top of the bulk valence band is identified with the maximum of the EDC of panel (c), i.e., the center of the “experimental stripe” of panel (b), a procedure we totally agree with.

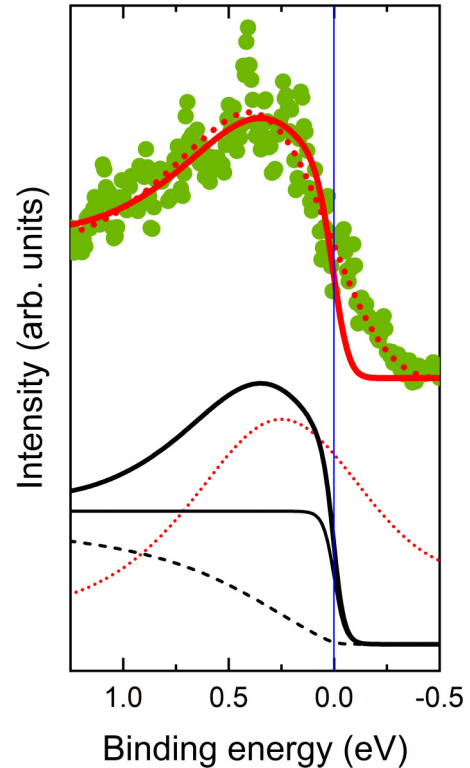


FIG. 2. Deconvolution of the EDC of Fig. 2(f). The fit is obtained by multiplying a Voigt function by the Fermi function (300 K), adding a Shirley-like background and finally convolving the result with a Gaussian (FWHM = 0.1 eV) to account for the experimental resolution. The result is shown in the upper part of the image as a red solid line superimposed to the data points (green dots). The red dotted line is the result of the same fit procedure, but here the FWHM of the final Gaussian has been set to 0.5 eV in the attempt to fit the part of the spectrum above E_f . The Voigt function [peak position 0.25 eV and full width at half maximum (FWHM) = 1.1 eV] is composed by a Lorentzian (FWHM = 1.0 eV) convolved with a Gaussian (FWHM = 0.4 eV). In the lower part of the image, the Voigt function is the red dotted line, the Fermi function (here multiplied by a factor of 50) is the black thin solid line, and the background is the black dashed line, while the combination of these functions is given by the black thick solid line.

step edges and would strongly enhance the broadening caused by impurity scattering for the π states ...” We agree with this interpretation and notice that indeed by comparing the peak in Fig. 2(f) with the magenta curve in Fig. 2(g), it appears that—after background subtraction and normalization to the same height—the two curves are practically identical. This finding cannot be a coincidence and reinforces our interpretation of the peak in Fig. 2(f) as due to photoemission from the K point.

The experimental data of Fig. 2(f) can be fitted with a Voigt function centered 0.25 eV below E_f . The result is shown in Fig. 2.

It is seen that the fit is fairly good everywhere except for energies above the Fermi level. This result points out that most of the photoemission signal above E_f is anomalous. In fact, the data show photoelectrons up to 0.3–0.4 eV above E_f , while the Fermi cutoff at $T = 300\text{ K}$ should reduce the signal to negligible levels ($< 2 \times 10^{-2}$) above 0.1 eV, and accounting

for the instrumental resolution (100 meV) does not change these figures significantly. Indeed, we were not able to fit the spectrum above E_f except by simulating the experimental resolution with a larger Gaussian (FWHM = 0.5 eV), although this procedure has no physical justification. Moreover, the goodness of the fit is almost independent from the position of the Voigt function, between 0.3 eV and 0.

Finally, we wish to comment on the disagreement of the present ARPES results with the previous ones. In [1] it is stated that “our ARPES measurements do not compare well with the experimental results presented by Graupner *et al.* (1997) and Himpfel *et al.* (1981). In their works, an energy gap of at least 0.5 eV between the maximum of the surface state at K and E_f is observed.” Since our interpretation of the data yields a photoemission gap of about 0.25 eV, the discrepancy between the old and the new ARPES measurements reduces from “at least 0.5 eV” to 0.25 eV. This small value can be explained by the different sensitivities of the apparatuses. Therefore, a substantial agreement is found of the present ARPES data with the previous ones. Moreover, this finding implies that the surface Fermi level was the same, or at least not very different, in the two samples, despite the different qualities of the surfaces. While in [1] it is suggested that there exist two kinds of diamond C(111)- 2×1 surfaces, one metallic and the other semiconducting, possibly depending on the flatness of the surface, according to our interpretation the diamond C(111)- 2×1 surface has always been one and the same throughout all the past and present investigations.

II. THEORETICAL PART

We agree the findings in Ref. [1] that real metallicity of the C(111)-(2×1) surface would be consistent with the theoretical electronic band structures of the ideal symmetric π -bonded-chain model, originally proposed by Pandey [9], computed at a Kohn-Sham density-functional theory (KS-DFT) level. As written in Ref. [1], “the most energetically favorable structural models suggest that symmetric π -bonded surface chains with little-to-no dimerization should occur [10–12], and that the resulting electronic structure should feature a metallic surface state that intersects the Fermi level (E_f).”

In support of their thesis the authors quote a ground-state DFT calculation, which can be compared with other DFT simulations of many years ago. However, it must be kept in mind that KS eigenvalues of DFT do not provide the proper theoretical framework when dealing with the band structure of any material. Instead, excited-state calculations using many-body theory are needed [13]. Generally speaking, KS eigenvalues can often be considered a valid starting point for perturbative GW calculations, but this is not the case of the present surface for which the DFT-KS approach provides an incorrect population of the surface bands requiring self-consistent GW calculations. Indeed, recent studies reconcile the “experimentally observed pronounced band gap” with the “ideal symmetric π -bonded-chain model, originally proposed by Pandey.” Reference [14] provides a semiconducting band structure for the C(111)-(2×1) surface, further confirmed in Ref. [15], giving a common description of the reconstructed surface from both an experimental and theoretical point of view.

In conclusion, we believe that the presented data, an interesting work within the wide panorama of research on the C(111)-(2×1) surface, are totally comparable with previous studies that showed a semiconducting character for this surface. Indeed, a careful inspection of their data reveals that ARPES spectra are in agreement with the numerous experimental data (obtained by photoemission, optical, and electron energy loss spectroscopies) proving the semiconducting character of this surface. Within an advanced theoretical formulation, the gap is foreseen and in good agreement with the experimental data.

ACKNOWLEDGMENT

One of the authors (G.B.) is grateful to A. Calloni (Politecnico di Milano) for useful discussion.

DATA AVAILABILITY

No data were created or analyzed in this study.

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