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Low-energy Electron Reflectivity from Graphene

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Abstract

Low-energy reflectivity of electrons from single- and multi-layer graphene is examined both theoretically and experimentally. A series of minima in the reflectivity over the energy range of 0 – 8 eV are found, with the number of minima depending on the number of graphene layers. Using first-principles computations, it is demonstrated that a free standing *n*-layer graphene slab produces $n-1$ reflectivity minima. This same result is also found experimentally for graphene supported on SiO_2. For graphene bonded onto other substrates it is argued that a similar series of reflectivity minima is expected, although in certain cases an additional minimum occurs, at an energy that depends on the graphene-substrate separation and the effective potential in that space.

The reflectivity of low-energy electrons from single- and multi-layer graphene has proven to be a very useful probe of the material. When examined over the energy range of about 0 – 8 eV, such spectra reveal a series of local maxima and minima. The minima in particular are important, since they reveal transmission maxima, i.e. *transmission resonances*, for the graphene. It was demonstrated in 2008 by Hibino et al. that, for *n* layers of graphene on a SiC(0001) surface, there are *n* minima in the spectra.[1] This relationship has provided the basis for subsequent works in which the thickness variation of the graphene on SiC is mapped out over the SiC wafer.[2,3,4,5,6] Hibino and co-workers presented a simple tight-binding model in which the transmission resonances arise from states localized on each graphene layer, with reflectivity minima formed by linear combination of those states. [1]

The reflectivity spectra for graphene on metal substrates are found to be, overall, similar to those for graphene on SiC. They reveal a series of minima in the energy range 0 – 8 eV, but now it is generally found that *n* layers of graphene produce $n-1$ minima in the reflectivity.[7,8,9] In this result, however, the layer of graphene closest to the substrate is *included* in the count of the number of layers, even though this layer might have electronic properties that deviate from those of graphene due to its bonding to the substrate (we refer to such a layer as *graphene-like*, i.e. with structure similar to that of graphene but with different electronic properties). Such a graphene-like layer also exists for the SiC(0001) surface, known as the "buffer layer",[10] and this graphene-like layer was *not included* in the layer count in the work of Hibino et al.[1] If we *do* include that layer, we then arrive at the result of $n-1$ reflectivity for *n* layers of graphene on SiC, the same as for graphene on metals. Utilization of this revised counting, however, begs the question of how the interface between graphene and the substrate should be properly treated in a full model for the reflectivity spectra.

In addition to this question, there are a number of "irregularities" in the reflectivity spectra that have been noted in recent works. For graphene on SiC(0001), if the graphene-like buffer layer is decoupled from the substrate (e.g. by hydrogenation) then an extra minimum is formed in the spectrum.[3] Depending on the detailed treatment used for the decoupling, this minimum can have a position similar to one of those in the original spectra, or at a higher energy.[5] The same behavior has been reported for graphene on the $\mathrm{SiC}(000\overline{1})$ surface, prepared in disilane, for which a graphene-like buffer layer also exists and can be decoupled from the SiC.[6] No theoretical understanding of the energetic locations of these additional minima presently exists.

In this work we develop a theoretical method for computing reflectivity spectra of graphene, and we compare those results with experimentally obtained spectra. For free-standing graphene we demonstrate that *n* layers of graphene actually produce $n-1$ minima in its reflectivity spectrum. The reason that $n-1$ minima are obtained, rather than *n*, is that the wavefunctions for the relevant scattering states are localized *in between* the graphene layers (not *on* them, as in the Hibino et al. model[1]). These states derive from the *interlayer band* of graphite, the structure of which depends sensitively on the exchange-correlation potential in the material.[11,12,13] In our work, we employ a relatively accurate description of that potential, in 3-dimensions, from which we derive the reflectivity of the low-energy electrons. We argue that the pattern of $n-1$ reflectance minima for *n*-layer graphene persists even when the bottommost graphene layer is strongly bonded onto a substrate. However, for a graphene layer that is more weakly bonded onto a substrate we argue that an additional reflectivity is sometimes formed, arising from an interlayer state formed in the space between the graphene and the substrate. The energy of this additional state is typically higher than those of the regular interlayer graphene states, and in this way, the above-mentioned irregularities in the observed spectra can be understood.

For our computations we use the Vienna Ab-Initio Simulation Package (VASP), employing the projector-augmented wave method and the generalized-gradient approximation for the density functional,[14,15,16] with a plane-wave energy cutoff of 500 eV. For graphite, we obtain a band structure which is identical to that displayed by Hibino et al.[1] For free-standing graphene, we simulate the graphene slab surrounded by vacuum of some thickness > 1 nm on either side of the slab. Labeling the direction normal to the slab as z, we form linear combinations of the wavefunctions for $k_z > 0$ and $k_z < 0$ such that the waves on one side of the slab have only outgoing character, i.e. an $\exp(+ik_z z)$ transmitted wave. Then, using the same linear combination on the other side of the slab permits us to determine the incident and reflected waves, from which we obtain the reflectivity. Details are provided in the Supplementary Material.

Results are shown in Fig. 1 for the reflectivity spectra of free-standing graphene. We find for an n-layer graphene slab (0.335 nm between layers) that there are $n-1$ minima in the reflectivity. The associated wavefunctions are peaked *in between* the graphene layers, as shown in Fig. 2 for the case of 4-layer graphene. These states derive from the image-potential states associated with graphene (all our computation contain two additional eigenvalues slightly *below* the vacuum level associated with symmetric and antisymmetric linear combinations of those states existing on both surfaces of the graphene slab).[17] For the three interlayer spaces displayed in Fig. 2 there are three interlayer states. These interlayer states couple together to form the three transmission resonances seen in the $n=4$ spectrum. Focusing on the real part of the wavefunctions in Fig. 2, the linear combinations are indicated by the labels "+", "0", or "$-$" on the wavefunction peaks, in accordance with a tight-binding scheme described in detail in Ref. [17].

The computed spectra of Fig. 1 show very good agreement with measured reflectivity curves for multilayer graphene on SiC and other substrates,[1,2,7,9] aside from the occasional presence of higher energy features in those spectra (e.g. with decoupled bottommost graphene layers as discussed in the introductory paragraphs above). However, one significant exception to this agreement occurs for the spectra of graphene on SiO_2 reported by Locatelli et al.[18] Those authors report similar results for free-standing graphene and for graphene supported on SiO_2. For a single layer of graphene on SiO_2 their spectrum displays no strong feature in the reflectivity, in agreement with the $n=1$ case of Fig. 1. However, their 2-layer spectrum displays two reflectivity minima and 3 layers displays three minima, in contradiction to the results of Fig. 1. This significant contradiction calls into question either the experimental or the theoretical results.

Due to this contradiction, we have conducted our own reflectivity measurements of single and multilayer graphene on SiO_2 using an Elmitec low-energy electron microscope (LEEM) III. Graphene was first grown on Cu foils by low-pressure chemical vapor deposition (CVD),[19] and then two of these graphene layers were sequentially transferred onto SiO_2 covered Si wafers.[20] Samples were cleaned by vacuum annealing for 8 hours at 340°C prior to LEEM study. Experimental electron reflectivity curves for 1 to 4 layers of graphene from these samples are shown in Fig. 3. The corresponding location for each spectrum is indicated in the LEEM image (inset). Identification of the number of layers is made on the basis of the preparation procedure and the resulting film morphology as described in Ref. [20]. For example, the top graphene layer used in this study was non-continuous leaving single-layer regions visible in LEEM images. Three- and four-layer regions come from folds and multilayer nuclei of CVD graphene.

For a single graphene layer we find a somewhat sloping reflectivity, but with no clear minimum. For 2 layers of graphene we find a single reflectivity minimum and for 3 layers we find two minima. We therefore find results which are in good agreement with the theoretical predictions of Fig. 1, at least for $n = 2$ and $n = 3$ (the energy positions of the minima differ slightly between experiment and theory, but these precise locations involve the separation and interaction between neighboring graphene layers, which could be influenced by residual extrinsic effects in the transferred graphene[21,22]). For the single-layer case the sloping reflectivity is not reproduced in the $n = 1$ theory, but this experimental result likely again depends in detail on residual interactions,[21] the corrugation between the substrate and the graphene as further discussed below, and/or the electron transmission of the LEEM due to a particular aperture setting (and, indeed, the spectrum for $n = 1$ in Ref. [18] appears much flatter). Our experimental result for $n = 2$, with a single well-defined reflectivity minimum, is in disagreement with the prior experimental work of Locatelli et al.[18] However, these same authors in a recent re-examination of their data have identified a spectrum with a single reflectivity minimum,[23] consistent with our interpretation.

The multilayer graphene utilized in our experiments actually consists of *twisted* layers (i.e. without Bernal stacking). Theoretically we expect that this type of twist will produce little change in the reflectivity spectra, since the distance between graphene planes does not change significantly and also the interlayer states that form between the planes have very little (<1%) modulation in their wavefunctions in the directions parallel to the planes. Indeed we find the reflectivity of a twisted bilayer with a $\sqrt{7} \times \sqrt{7}$ - $R38.2^\circ$ structure differs from that of untwisted graphene by less than 0.03 over the entire energy range examined.

We now turn to briefly consider the situation for graphene on a substrate. So long as the bottommost graphene layer that is bonded to the substrate is not so severely distorted as to affect the separation (bonding) between it and the next higher graphene layer, then we expect the spaces between the graphene planes (and the potential therein) will be essentially the same as for free-standing multilayer graphene. Therefore we expect a similar set of interlayer states for the two situations. The only additional consideration is whether or not the space between the bottommost graphene layer and the substrate can itself support an interlayer state. For a relatively small separation d between the bottommost graphene layer and the substrate (i.e. graphene that is strongly bonded to the substrate), we do not expect an interlayer state to form. We have made explicit computations of this situation by considering graphene on Cu(111), using a generalization of the above theoretical methods that will be described elsewhere.[24] We do indeed find that for $d \leq 0.25$ nm the reflectivity spectra are essentially identical for free-standing graphene compared to graphene on the substrate; in both cases there are $n-1$ reflectivity minimum for n-layer graphene (including the bottommost graphene-like layer in the count).

For larger d values, i.e. more weakly bound graphene on the substrate, an additional reflectivity minimum occurs in the spectrum, with an energy that decreases as the separation d increases.[24]

For example, at $d = 0.30$ nm this minimum occurs at 9.4 eV whereas for $d = 0.35$ nm it is at 5.1 eV (smaller separations produce confinement of the state, hence shifting it to higher energies). A single layer of graphene on SiO_2 might be expected to display this type of reflectivity minimum, but the significant corrugation of the graphene is likely sufficient to inhibit the formation of an interlayer state.[18,25] These numerical results for the energies will vary somewhat depending on the particular substrate, i.e. on the effective potential between the substrate and the bottommost graphene plane. In any case, a qualitative picture for the higher energy "irregular" features that are observed in the experiments emerges from our analysis: an interlayer state can be produced between a weakly bonded (e.g. decoupled) bottommost graphene layer and the substrate. This interlayer state couples to its neighbors, producing an additional reflectivity minimum. Experimentally, this extra minimum is often found to occur at somewhat higher energies compared to the regular series arising from the graphene-graphene separations, presumably because the value of d is somewhat less than a the graphene-graphene spacing of 0.335 nm (and/or the effective potential is higher than that between graphene planes). The situation for graphene decoupled from SiC(0001) by a hydrogenation appears to be a special one in which, coincidentally, the energy of the interlayer state that forms between the decoupled graphene layer and the substrate turns out to be nearly the same as the energy of a graphene-graphene interlayer state.

In summary, we have presented first-principle theoretical results for low-energy reflectivity spectra from free-standing graphene, and compared those to experiment. Good agreement is found (utilizing new experimental results). For n-layer graphene, $n-1$ minima occur in the reflectivity spectra over 0 – 8 eV, with these minima being associated with interlayer states that form between the graphene planes. Multilayer graphene with the bottommost layer strongly bonded to a substrate yields a very similar spectra as for the free-standing case. For graphene that is more weakly bonded to a substrate an additional minimum in the reflectivity occur under certain conditions, with an energy that depends on the separation and effective potential between the substrate and the graphene.

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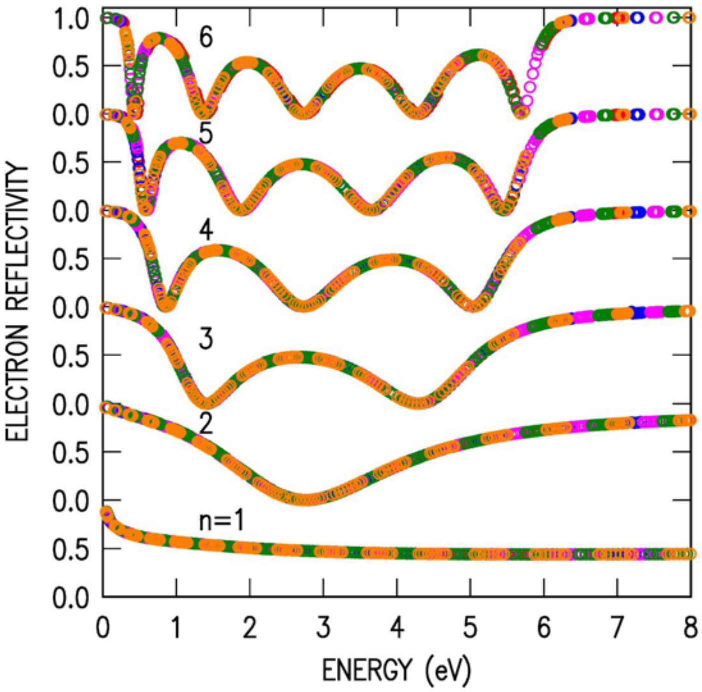

FIG 1. (Color on-line) Computed reflectivity for free-standing slabs of *n*-layer graphene. For each *n,* a series of computation are performed with different vacuum widths; differently shaded (colored) data points are used for plotting the results for each width.

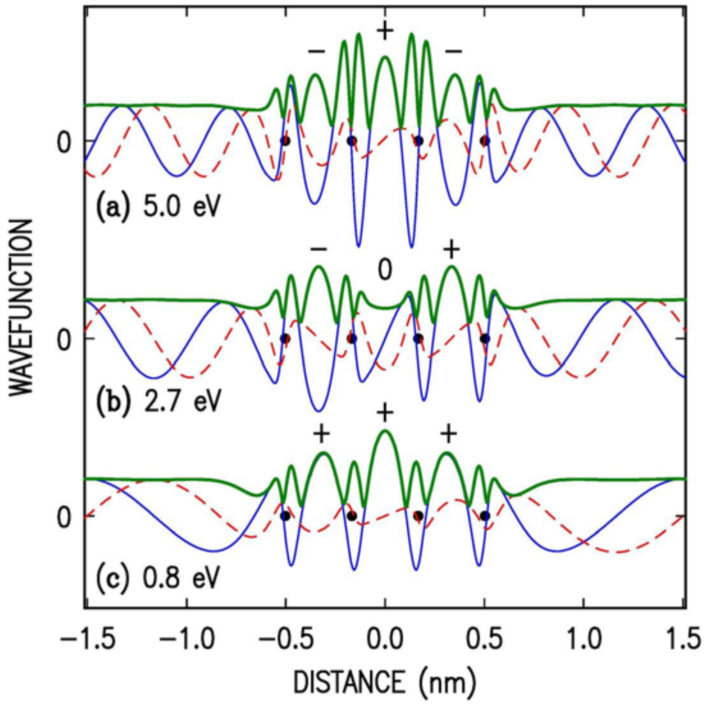

FIG 2. (Color on-line) Wavefunctions at the energies of transmission resonances for $n = 4$ layers of free-standing graphene. The real part of the wavefunction is shown by the thin solid line, the imaginary part by the thin dashed line, and the magnitude by the thick solid line (blue, red, and green, respectively, in the color version). The solid black dots indicate the positions of the graphene layers. The +, –, and 0 symbols indicate peaks in the wavefunctions that are concentrated between the graphene layers.

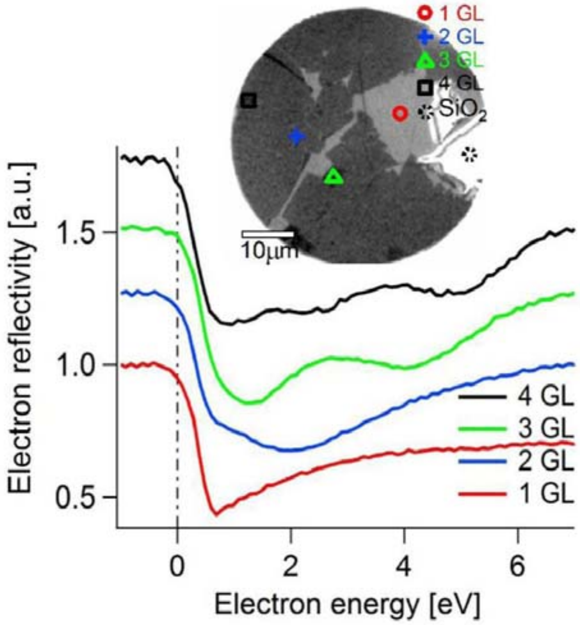

FIG 3. (Color on-line) Measured electron reflectivity for single and multiple graphene layers (GL) on SiO_2; curves are vertically offset for clarity. The LEEM image in the inset (acquired at energy 1.8 eV above the sample's vacuum level) shows the surface from where the reflectivity spectra were acquired.

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