Making graphene visible

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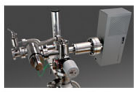
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Making graphene visible

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Microfabrication of graphene devices used in many experimental studies currently relies on the fact that graphene crystallites can be visualized using optical microscopy if prepared on top of Si wafers with a certain thickness of SiO_2. The authors study graphene's visibility and show that it depends strongly on both thickness of SiO_2 and light wavelength. They have found that by using monochromatic illumination, graphene can be isolated for any SiO_2 thickness, albeit 300 nm (the current standard) and, especially, $\approx$100 nm are most suitable for its visual detection. By using a Fresnel-law-based model, they quantitatively describe the experimental data. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2768624]

Since it was reported in 2004,[1] graphene—a one-atom-thick flat allotrope of carbon—has been attracting increasing interest.[1–3] This interest is supported by both the realistic promise of applications and the remarkable electronic properties of this material. It exhibits high crystal quality, ballistic transport on a submicron scale (even under ambient conditions) and its charge carriers accurately mimic massless Dirac fermions.[2–4] Graphene samples currently used in experiments are usually fabricated by micromechanical cleavage of graphite: a euphemism for slicing this strongly layered material by gently rubbing it against another surface.[5] The ability to create graphene with such a simple procedure ensures that graphene was produced an uncountable number of times since graphite was first mined and the pencil invented in 1565.[6]

Although graphene is probably produced every time one uses a pencil, it is extremely difficult to find small graphene crystallites in the "haystack" of millions of thicker graphitic flakes which appear during the cleavage. In fact, no modern visualization technique (including atomic-force, scanning-tunneling, and electron microscopies) is capable of finding graphene because of their extremely low throughput at the required atomic resolution or the absence of clear signatures distinguishing atomic monolayers from thicker flakes. Even Raman microscopy, which recently proved itself as a powerful tool for distinguishing graphene monolayers,[7] has not yet been automated to allow search for graphene crystallites. Until now, the only way to isolate graphene is to cleave graphite on top of an oxidized Si wafer and then carefully scan its surface in an optical microscope. Thin flakes are sufficiently transparent to add to an optical path, which changes their interference color with respect to an empty wafer.[1] For a certain thickness of SiO_2, even a single layer was found to give sufficient, albeit feeble, contrast to allow the huge image-processing power of the human brain to spot a few micron-sized graphene crystallites among copious thicker flakes scattered over a millimeter-sized area.

So far, this detection technique has been demonstrated and widely used only for a SiO_2 thickness of 300 nm (purple-to-violet in color), but a 5% change in the thickness (to 315 nm) can significantly lower the contrast.[2] Moreover, under nominally the same observation conditions, graphene's visibility strongly varies from one laboratory to another (e.g., see images of single-layer graphene in Refs. 1 and 4), and anecdotal evidence attributes such dramatic differences to different cameras, with the cheapest ones providing better imaging.[8] Understanding the origin of this contrast is essential for optimizing the detection technique and extending it to different substrates, aiding experimental progress in the research area.

In this letter, we discuss the origin of this optical contrast and show that it appears due not only to an increased optical path but also to the notable opacity of graphene. By using a model based on the Fresnel law, we have investigated the dependence of the contrast on SiO_2 thickness and light wavelength λ, and our experiments show excellent agreement with the theory. This understanding has allowed us to maximize the contrast and, by using narrow-band filters, to find graphene crystallites for practically any thickness of SiO_2 and also on other thin films such as Si_3N_4 and polymethyl methacrylate (PMMA).

Figure 1 illustrates our main findings. It shows graphene viewed in a microscope [Nikon Eclipse LV100D with a 100×, 0.9 numerical aperture (NA) objective] under normal, white-light illumination on top of a Si wafer with the standard 300 nm thickness of SiO_2 [Fig. 1(a)]. For comparison, Fig. 1(c) shows a similar sample but on top of 200 nm SiO_2, where graphene is completely invisible. In our experience, only flakes thicker than ten layers could be found in white light on top of 200 nm SiO_2. Note that the ten-layer thickness also marks the commonly accepted transition from graphene to bulk graphite.[2] Top and bottom panels in Fig. 1 show the same samples but illuminated through various narrow-band filters. Both flakes are now clearly visible. For 300 nm SiO_2, the main contrast appears in green [see Fig. 1(b)], and the flake is undetectable in blue light. In

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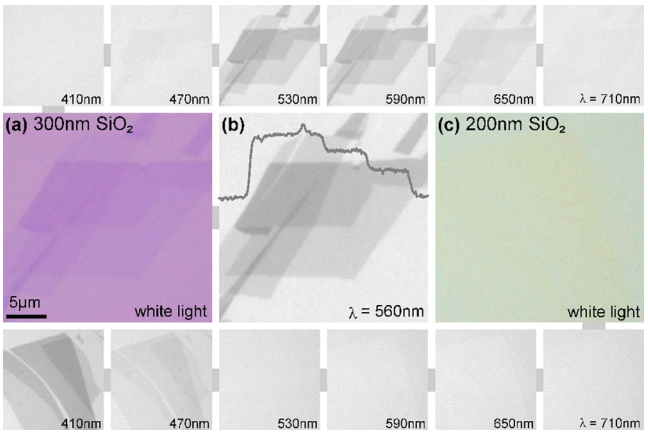

FIG. 1. (Color online) Graphene crystallites on 300 nm SiO_2 imaged with white light (a), green light and another graphene sample on 200 nm SiO_2 imaged with white light (c). Single-layer graphene is clearly visible on the left image (a), but even three layers are indiscernible on the right (c). Image sizes are 25×25 μm^2. Top and bottom panels show the same flakes as in (a) and (c), respectively, but illuminated through various narrow bandpass filters with a bandwidth of $\simeq$10 nm. The flakes were chosen to contain areas of different thickness so that one can see changes in graphene's visibility with increasing numbers of layers. The trace in (b) shows steplike changes in the contrast for 1, 2, and 3 layers (trace averaged over 10 pixel lines). This proves that the contrast can also be used as a quantitative tool for defining the number of graphene layers on a given substrate.

comparison, the use of a blue filter makes graphene visible even on top of 200 nm SiO_2 (see lower panels).

To explain the observed contrast, we consider the case of normal light incidence from air (refractive index $n_0=1$) onto a trilayer structure consisting of graphene, SiO_2, and Si (see inset of Fig. 2). The Si layer is assumed to be semi-infinite and characterized by a complex refractive index $n_3(\lambda)$ that, importantly, is dependent on λ [for example, $n_3(\lambda=400\ \text{nm})\approx5.6-0.4i$].[9] The SiO_2 layer is described by thickness d_2 and another λ-dependent refractive index $n_2(\lambda)$ but with a real part only[9] [$n_2(400\ \text{nm})\approx1.47$]. We note that these $n_2(\lambda)$ and $n_3(\lambda)$ accurately describe the whole range of interference colors for oxidized Si wafers.[10] Single-layer graphene is assumed to have a thickness d_1 equal to the extension of the π orbitals out of plane[11] ($d_1=0.34$ nm) and a complex refractive index $n_1(\lambda)$. While $n_1(\lambda)$ can be used in our calculations as a fitting parameter, we avoided this uncertainty after we found that our results were well described by the refractive index of bulk graphite $n_1(\lambda)\approx2.6-1.3i$, which is independent of λ.[9,12] This can be attributed to the fact that the optical response of graphite with the electric field parallel to graphene planes is dominated by the in-plane electromagnetic response.

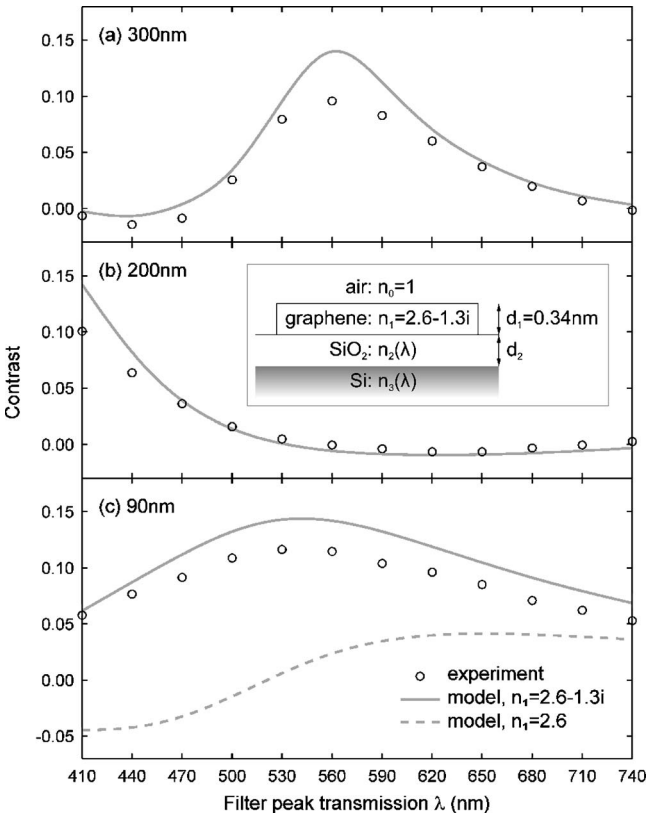

FIG. 2. Contrast as a function of wavelength for three different thicknesses of SiO_2. Circles are the experimental data; curves the calculations. Inset: the geometry used in our analysis.

Using the described geometry, it is straightforward to show that the reflected light intensity can be written as:[13]

$$I(n_1)=\left|(r_1e^{i(\Phi_1+\Phi_2)}+r_2e^{-i(\Phi_1-\Phi_2)}+r_3e^{-i(\Phi_1+\Phi_2)}+r_1r_2r_3e^{i(\Phi_1-\Phi_2)})\times(e^{i(\Phi_1+\Phi_2)}+r_1r_2e^{-i(\Phi_1-\Phi_2)}+r_1r_3e^{-i(\Phi_1+\Phi_2)}+r_2r_3e^{i(\Phi_1-\Phi_2)})^{-1}\right|^2, \quad (1)$$

where

$$r_1=\frac{n_0-n_1}{n_0+n_1},$$

$$r_2=\frac{n_1-n_2}{n_1+n_2},$$

$$r_3=\frac{n_2-n_3}{n_2+n_3} \quad (2)$$

are the relative indices of refraction. $\Phi_1=2\pi n_1d_1/\lambda$ and $\Phi_2=2\pi n_2d_2/\lambda$ are the phase shifts due to changes in the optical path. The contrast C is defined as the relative intensity of reflected light in the presence ($n_1\neq1$) and absence ($n_1=n_0=1$) of graphene,

$$C=\frac{I(n_1=1)-I(n_1)}{I(n_1=1)}. \quad (3)$$

For quantitative analysis, Fig. 2 compares the contrast observed experimentally with the one calculated by using Eq. (3). The experimental data were obtained for single-layer graphene on top of SiO_2/Si wafers with three different SiO_2 thicknesses by using 12 different narrow-band filters. One can see excellent agreement between the experiment and theory. The contrast reaches up to $\simeq$12%, and the peaks in graphene's visibility are accurately reproduced by our model.[14] Note, however, that the theory slightly but systematically overestimates the contrast. This can be attributed to deviations from normal light incidence (because of high NA) and an extinction coefficient of graphene, $k_1=-\text{Im}(n_1)$, that may differ from that of graphite. k_1 affects the contrast both by absoption and by changing the phase of light at the interfaces, promoting destructive interference. To emphasize the important role played by this coefficient, the dashed line in Fig. 2(c) shows the same calculations but with $k_1=0$. The

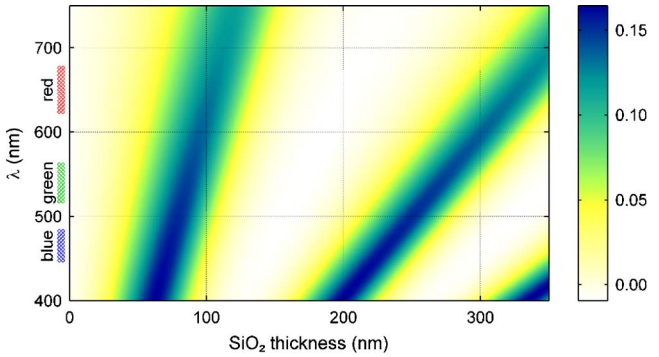

FIG. 3. (Color online) Color plot of the contrast as a function of wavelength and SiO_2 thickness according to Eq. (3). The color scale on the right shows the expected contrast.

latter curve does not bare even a qualitative similarity to the experiment, which proves the importance of opacity for the visibility of graphene.

To provide a guide for the search of graphene on top of SiO_2/Si wafers, Fig. 3 shows a color plot for the expected contrast as a function of SiO_2 thickness and wavelength. This plot can be used to select filters most appropriate for a given thickness of SiO_2. It is clear that by using filters, graphene can be visualized on top of SiO_2 of practically any thickness, except for $\approx$150 nm and below 30 nm. Note, however, that the use of green light is most comfortable for eyes that, in our experience, become rapidly tired with the use of high-intensity red or blue illumination. This makes SiO_2 thicknesses of approximately 90 and 280 nm most appropriate with the use of green filters as well as without any filters, in white light. In fact, the lower thickness of $\simeq$90 nm provides a better choice for graphene's detection (see Fig. 2), and we suggest it as a substitute for the present benchmark thickness of $\simeq$300 nm.

Finally, we note that the changes in the light intensity due to graphene are relatively minor, and this allows the observed contrast to be used for measuring the number of graphene layers (theoretically, multilayer graphene can be modeled by the corresponding number of planes separated by d_1). The trace in Fig. 1(a) shows how the contrast changes with the number of layers, and the clear quantized plateaus show that we have regions of single, double, and triple layer graphene. Furthermore, by extending the same approach to other insulators, we were able to find graphene on 50 nm Si_3N_4 using blue light and on 90 nm PMMA using white light.

In summary, we have investigated the problem of visibility of graphene on top of SiO_2/Si wafers. By using the Fresnel theory, we have demonstrated that contrast can be maximized for any SiO_2 thickness by using appropriate filters. Our work establishes a quantitative framework for detecting single and multiple layers of graphene and other two-dimensional atomic crystals[5] on top of various substrates.

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