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Optical contrast and clarity of graphene on an arbitrary substrate

Xuefeng Wang,[a)] Ming Zhao, and David D. Nolte[b)]
Department of Physics, Purdue University, West Lafayette, Indiana 47907, USA

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A molecularly thin dielectric film on a multilayer substrate can be treated as an additive perturbation of the substrate reflection coefficient r, for which the perturbation depends only on r and the optical properties of the film. This general result is applied to the problem of graphene on arbitrary substrates that seek to maximize the film contrast. We define clarity to describe the graphene image quality in the presence of charge-coupled device noise. A substrate with $r=1$ produces the highest graphene clarity in most practical situations. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3212735]

Optical microscopy is the most efficient tool to locate and identify graphene on a smooth substrate for graphene production and experiments. The contrast between graphene and the background is the crucial factor for graphene identification, and the contrast is small due to the ultrathin nature of graphene [thickness is 0.335 nm (Refs. 1–3)]. Considerable effort has been expended to improve the contrast on specific substrates (silicon dioxide,[4–6] silicon nitride,[7] and silicon carbide,[8] among others[9,10]). These studies are all based on explicit models of the substrates. In this paper, we derive a fundamental expression for the contrast of a film (graphene in this paper) on an arbitrary substrate with an original reflection coefficient r, which becomes r' after depositing the film. We find that r' is determined solely by r and by the optical properties of the film. The details of the substrate structure are not required to derive r'. This finding allows us to identify the value r of the substrate that optimizes either the contrast or the clarity for graphene imaging.

The equations derived here apply to any ambient medium, any incidence angle, and a film with complex refractive index. We also derive a concise equation to describe contrast that is not limited to graphene but can be applied to other thin film studies as well. Contrast is not always the most appropriate parameter to determine the quality of graphene images in practice. The property we call clarity can be defined to describe graphene images in the presence of noise, and we find what value of r optimizes the clarity.

The transfer matrix method[11] is used to calculate the Fresnel reflection coefficient r of an arbitrary n-layer substrate, illustrated in Fig. 1. When a film with thickness d and refractive index n_g is applied on the substrate, the new reflection coefficient r' is[12]

$$r' = \frac{(e^{i\delta_g} - e^{-i\delta_g})r_{0,g} + r(e^{-i\delta_g} - r_{0,g}^2 e^{i\delta_g})}{(e^{i\delta_g} - r_{0,g}^2 e^{-i\delta_g}) + r(e^{-i\delta_g} - e^{i\delta_g})r_{0,g}} e^{2i(\tan\theta_g/\tan\theta_0)\delta_g}, \tag{1}$$

which is rigorous without approximation. The only information needed from the substrate is the original r. Therefore, r' is a function of r and of the applied film, without any need for detailed information about the substrate structure. In Eq. (1), θ_0 is the incident angle and θ_g is the refraction angle in graphene with the relation of $n_g \sin\theta_g = n_0 \sin\theta_0$, where n_0 and n_g are the refractive indices of the ambient medium and graphene, respectively. Mostly $n_0=1$ because the graphene is usually imaged in air. $\delta_g = 2\pi n_g \cos\theta_g d/\lambda$, where d is the graphene thickness. $r_{0,g}$ is the reflection of the interface between the ambient medium and graphene. Under the condition of $d \ll \lambda$, Eq. (1) is simplified to

$$r' = r + 2i\delta_g\left[\frac{(r_{0,g}-r)(1-rr_{0,g})}{(1-r_{0,g}^2)} + r\left(\frac{\tan\theta_g}{\tan\theta_0}\right)\right]. \tag{2}$$

For s-polarization and at any incidence angle where $r_{0,g} = \sin(\theta_g - \theta_0)/\sin(\theta_g + \theta_0)$, Eq. (2) is expressed as

$$r' = r + \frac{(1+r)^2}{\cos\theta_0}\frac{(n_0^2 - n_g^2)}{n_0}\frac{\pi i}{\lambda}d. \tag{3}$$

For p-polarization, the final expression is more complicated and it is not presented here. Based on Eq. (3), the reflectance change $\Delta R = R' - R = |r'|^2 - |r|^2$ due to graphene is

$$\Delta R = \mathrm{Im}\left[\frac{(n_g^2 - n_0^2)}{n_0}\bar{r}(1+r)^2\right]\frac{2\pi d}{\lambda\cos\theta_0} \tag{4}$$

and the contrast $\Delta R/R$ is

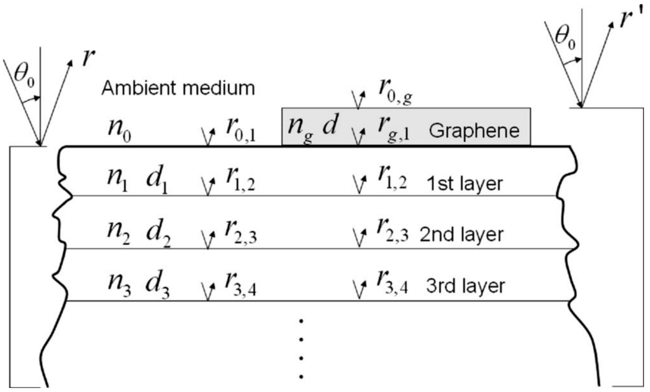

FIG. 1. The reflection coefficient r of a Bragg-stack substrate is determined by all interfaces, calculated by the transfer matrix method derived from Fresnel's law. When a film is on the substrate, the film plus substrate has a reflection r'. The new r' is explicitly determined by the original r and by the optical properties of the film and requires no explicit structure of substrate. Note that both r' and r are calculated with the same reference plane which is the surface of the substrate.

[a)] Electronic mail: wang137@purdue.edu.

[b)] Author to whom correspondence should be addressed. Electronic mail: nolte@physics.purdue.edu.

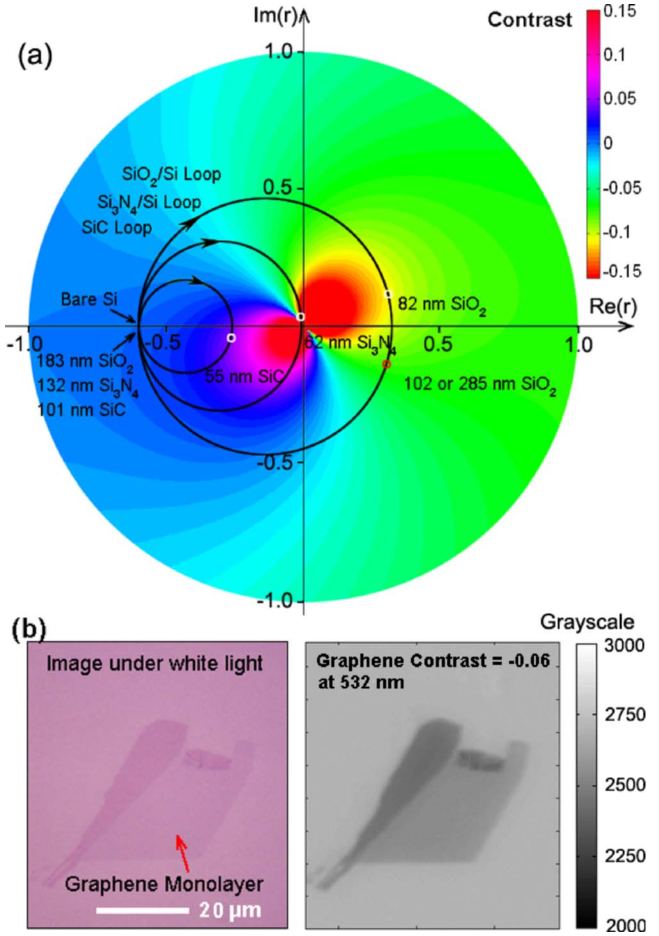

FIG. 2. (Color online) (a) Contrast map of graphene on the complex plane defined by the complex r. This map shows the contrast of graphene on an arbitrary substrate with reflection coefficient r at the wavelength 532 nm and at normal incidence. The r for SiO_2/Si, Si_3N_4/Si, and SiC/Si (from outer ring to inner ring) substrates evolves in circles as the thickness of the supporting layer increases with periods of 183, 132, and 101 nm, respectively. The white dots on the circles indicate the SiO_2/Si oxide thickness that maximizes the absolute value of the contrast. (b) The contrast of graphene on a 285 nm SiO_2/Si substrate was measured to be -0.06 under 532 ± 5 nm light. The red dot on the SiO_2/Si circle in (a) indicates a contrast -0.063 for graphene on a 285 nm SiO_2/Si substrate.

$$C = \frac{\Delta R}{R} = \frac{\Delta R}{r \cdot \bar{r}} = \mathrm{Im}\left[\frac{(n_g^2 - n_0^2)}{n_0}\frac{(1+r)^2}{r}\right]\frac{2\pi d}{\lambda \cos \theta_0}. \tag{5}$$

The approximation that d/λ is a small quantity compared to r is usually satisfied for graphene studies.

Equation (5) describes graphene contrast on an arbitrary substrate with an original reflection r in a concise form enabling a convenient theoretical analysis of the contrast of thin films. The complex refractive index n_g of graphene is contained separately in $(n_g^2 - n_0^2)/n_0$, where n_0 is the refractive index of the ambient medium, while r is separately contained in $(1+r)^2/r$. This equation can serve as a golden rule for the contrast calculation of a thin film on a substrate under the situation that $d/\lambda \ll |r|$, and that light is incident at normal angle or with s-polarization, which is usually valid in practice.

We calculate the contrast of graphene for all r based on Eq. (5). The contrast map is presented in Fig. 2 on the complex plane. The conditions are normal incidence, 532 nm wavelength, and air ambient. The refractive index of graphene is $n_g = 2.4 - 1.0i$ (Ref. 13) and the thickness is 0.335 nm. The absolute value of contrast becomes large when $|r|$ is small and when the phase of r is approximately $\pi/6$. The contrast goes to infinity when r goes to zero, as shown in Fig. 2(a). Contrast maps can also be acquired for other probe wavelengths and incidence angles based on Eq. (5).

The simplest substrate that gives graphene high contrast is thermal oxide on silicon. The trajectory of r on SiO_2/Si as a function of oxide thickness is a perfect circle as the SiO_2 thickness increases. The r circle evolves evenly as the SiO_2 thickness grows with a period of 183 nm at a wavelength of 532 nm. This phenomenon is also applied to other one-layer models including generally adopted Si_3N_4/Si and SiC/Si substrates used for graphene studies, with periods of 132 and 101 nm, respectively, at 532 nm wavelength. The complex trajectories are drawn in Fig. 2(a). The optimized positions where the absolute value of contrast is maximized [indicated by white dots in Fig. 2(a)] match the results from other specific model-based studies.[4,7,8] We tested the precision of the map with a graphene sample [purchased from Graphene Industries Co., Fig. 2(b)] made from highly oriented pyrolytic graphite. The substrate is 285 nm SiO_2 grown on Si with a calculated reflection coefficient $r = 0.27 - 0.21i$. The graphene was imaged by microscope under green light (530 ± 15 nm photodiode as the light source, filtered by a 532 ± 5 nm bandpass filter). The measured contrast is -0.06 which is close to the contrast value of -0.063 on the map. [The red dot on the SiO_2/Si circle in Fig. 2(a) indicates the position of this sample in the contrast map.]

Contrast goes to infinity when r approaches zero, and it would seem that the graphene can been seen most clearly on a zero-reflection (antireflection) substrate. However, the signal-to-noise ratio (SNR) determines how clearly graphene can be "seen," where the SNR is defined as the ratio of the net signal value to the root mean square noise of background. For a thin film deposited on a substrate with reflectance R, the net signal (e.g., from graphene) is $P_0 \Delta R$, where P_0 is the photon power received by 1 pixel in one image frame when the substrate has unity reflectance. P_0 is the product of the light intensity on the charge-coupled device (CCD) chip, the area of 1 pixel, and the integration time. The main CCD noise sources include dark current noise, on-chip read noise, off-chip digitization error, and shot noise. Shot noise depends on power as $N_S = \sqrt{\alpha P_0 R}$, where α is the CCD quantum yield divided by photon energy. All other noise sources are power independent and therefore they are background noise denoted as N_0. Shot noise and background noise are spatially and temporally uncorrelated, and the total noise is the quadrature summation $N = \sqrt{N_0^2 + \alpha P_0 R}$. The SNR is

$$\frac{P_0 \Delta R}{\sqrt{N_0^2 + \alpha P_0 R}} = \sqrt{\frac{P_0}{\alpha}}\frac{\Delta R}{\sqrt{N_0^2/\alpha P_0 + R}} = \sqrt{\frac{P_0}{\alpha}}\frac{\Delta R}{\sqrt{X + R}}$$

$$= \sqrt{\frac{P_0}{\alpha}} C_L. \tag{6}$$

We define $C_L = \Delta R/\sqrt{X+R}$ as the clarity of the graphene image where $X = N_0^2/\alpha P_0$ is the square of the ratio of the CCD background noise to shot noise. To improve the clarity of the graphene image, $\Delta R/\sqrt{X+R}$ should be maximized. X is determined by the light intensity, by the integration time and by the inherent quality of a CCD. X ranges from 1:0 to about 1:1000 for a typical CCD. In the experiment shown in

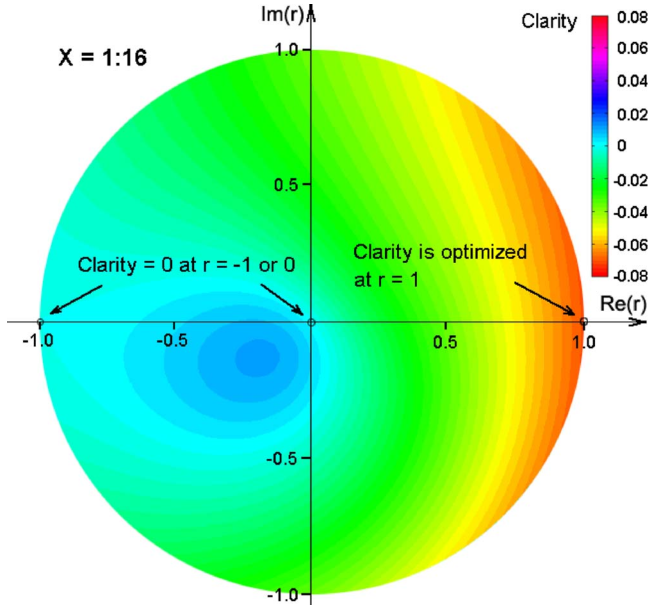

FIG. 3. (Color online) Clarity map of graphene on the complex plane for $X=1:16$. Taking the CCD noise into account, clarity [defined in Eq. (6)] is more appropriate than contrast to describe the quality of a graphene image. Clarity depends on X, which is the square of the ratio of CCD static noise to shot noise. X ranges from 1:0 to 1:100 in many practical situations and typically $X=1:16$. Clarity is optimized on a substrate with $r=1$.

Fig. 2(a), X is 1/16. The map of the clarity at this condition is shown in Fig. 3. Clarity vanishes at $r=-1$ or $r=0$ and clarity is optimized at $r=1$. Further calculation shows that clarity is optimized at $r=1$ in the full range of X from 1:0 to 1:1000. Therefore, a substrate with $r=1$ provides the highest SNR and, therefore, the best image quality for graphene imaging in most applications. On such a substrate, a reflectance change $\Delta R=16\pi nkd/\lambda=0.076$, where n and k are the real and the imaginary parts of n_g, reaches a maximum among all substrates. As another advantage of a substrate with $r=1$, a lossless dielectric thin film ($k=0$ for such a film) with subwavelength thickness becomes completely invisible on such a substrate. Therefore, surface roughness on the substrate contributes little noise to the image. A substrate with $r=1$ can be relatively economically fabricated by coating a Bragg stack on a glass surface. It is worth to mention that for microscopes equipped with high numeric-aperture (NA) objective lens, the incident light has an angular intensity distribution. The average contrast and clarity can be acquired by integrating the contrast or clarity function over the incident angle and the angular distribution of light intensity is the weighting factor. Even so, high NA lens causes little impact to the conclusion that $r=1$ substrate produces best graphene images because the $r=1$ Bragg stack has considerable angle tolerance and clarity of graphene is prevalently high in the region around $r=1$ (Fig. 3).

In summary, we have shown that graphene modifies r of the substrate to r' independently of the substrate structure, and r' is determined only by the original r. The equation for r' was derived with r as a variable and the contrast of graphene is analytically expressed as a function of r. This equation enables the discussion of graphene contrast on arbitrary substrates without a need for specific models of the substrate. We also emphasize clarity to describe how r optimizes the SNR of the graphene image in the presence of CCD noise. One direct conclusion is that graphene can be seen most clearly on a substrate with $r=1$ where both clarity and the reflectance change due to graphene reach a maximum among all possible substrates.

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