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Colors of graphene and graphene-oxide multilayers on various substrates

Inhwa Jung¹, Jong-Soo Rhyee², Jong Yeog Son², Rodney S Ruoff³ and Kyong-Yop Rhee¹

¹ Department of Mechanical Engineering, Kyung Hee University, Suwon 446-701, Korea
² Department of Applied Physics, College of Applied Science, Kyung Hee University, Suwon 446-701, Korea
³ Department of Mechanical Engineering, University of Texas at Austin, Austin, TX 78712-0292, USA

E-mail: jyson@khu.ac.kr and r.ruoff@mail.utexas.edu

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Abstract
We investigated the colors of graphene and graphene-oxide multilayers that were deposited on various dielectric layers. In particular, the effects of the material thickness, the types of dielectric layers, and the existence of a back silicon substrate were analyzed. The colors of graphene-oxide layers on a SiO₂/Si substrate were found to periodically change as the material thickness increased. However, the colors of graphene layers on the same substrate became saturated without a similar periodic change. The calculated colors corresponding to the material thicknesses were verified by optical microscopy and profilometry. We believe that these results demonstrate the possibility of utilizing color as a simple tool for detecting and estimating the thicknesses of graphene and graphene-oxide multilayers.

1. Introduction

Graphene is a monolayer of graphite, whose sheets have an interplanar spacing of 0.34 nm. This thin layer of carbon has a high optical transmittance and electrical conductivity, making it favorable for use in optoelectronic applications [1–4]. In addition, graphene has excellent physical properties in mechanical strength [5], thermal conductivity [6, 7], and high electron mobility [8]. These advantages place graphene as one of most promising emergent materials of the future. In order to obtain layers of graphene, they are exfoliated mechanically either from graphite [9, 10] or by chemical oxidation [13], or they are synthesized by chemical vapor deposition (CVD) [11] or epitaxial growth [12]. Chemical oxidation, in particular, is an inexpensive way of obtaining graphene, but the process alters the structure of graphene by oxidizing it, creating graphene-oxide. Conveniently, this chemically modified graphene is useful for creating films deposited on substrates [3] or as filler for composite [14] or paper-like materials [15].

With the development of graphene technology, it has become important to visualize and determine the thickness of the deposited graphene layers. Atomic force microscopy (AFM) and micro-Raman spectroscopy are reliable methods of doing so; however, these techniques require a long measurement time [16]. In contrast, optical microscopy offers a fast imaging speed over a large area [9, 10, 17–20], but it requires proper selection of dielectric layers with optimized thicknesses in order to maximize the visibility of the graphene layers [21]. In particular, color charts can be used as a fast and intuitive way to visualize the graphene layers and obtain information about multilayered systems [22]. In previous studies, the colors of graphene multilayers on SiO₂/Si substrates were generated using thin film optics, and were verified by optical microscopy and AFM measurements [20], and the mechanisms behind the visibility of graphene were discussed. The effect of the dielectric layers—e.g., silicon dioxide (SiO₂), silicon nitride (Si₃N₄), and aluminum oxide (Al₂O₃)—was more thoroughly studied by Gao et al [23]. They employed the total color difference (TCD) method in order to evaluate the difference between the color of
the graphene layer and the underlying substrate. Using this method, one can determine the most efficient dielectric layer (and its thickness) for maximizing the visibility of a graphene multilayer.

Hence, we theoretically investigated the colors of graphene and graphene-oxide multilayers, as well as a few-layer graphene-oxide stack, deposited on various substrates. The colors were calculated based on the optical reflectance and transmittance using the thin film optics theory [24, 25].

2. Theory

Figure 1 shows a schematic drawing of the optical beam reflection and transmission for a graphene multilayer system. The system is composed of four layers: an air layer (incident medium), a graphene or graphene-oxide layer (top layer), a dielectric layer (middle layer), and a Si substrate or air layer (bottom layer). To calculate the optical reflectance and transmittance, we followed the matrix assembly method [24]. In this method, the electric and magnetic fields at the interface between the incident medium and the top layer \((E_a, H_a)\) are determined by multiplying the characteristic matrix of each layer (the top layer and middle layer) with the electric and magnetic fields at the interface between the middle layer and the bottom layer \((E_c, H_c)\), such that

\[
\begin{align*}
E_a &= \begin{bmatrix}
\cos \delta_1 & (i \sin \delta_1)/n_1 \\
-i n_1 \sin \delta_1 & \cos \delta_1
\end{bmatrix} E_c \\
H_a &= \begin{bmatrix}
\cos \delta_2 & (i \sin \delta_2)/n_2 \\
-i n_2 \sin \delta_2 & \cos \delta_2
\end{bmatrix} H_c
\end{align*}
\]

where the subscripts 1 and 2 denote the top layer and the middle layer, respectively. \(\delta\) is the phase factor, which is expressed as \(\delta = 2\pi N d \cos \theta/\lambda\), in which \(N\) is the optical constant, \(d\) is the layer thickness, \(\lambda\) is the wavelength of incident light, \(n\) is the admittance of the layer, and \(\theta\) is the beam angle. Further details can be found in [24]. The optical reflectance and transmittance can then be expressed as follows:

\[
R = \left( \frac{\eta_0 E_a/E_c - H_a/E_c}{\eta_0 E_a/E_c + H_a/E_c} \right) \left( \frac{\eta_0 E_a/E_c - H_a/E_c}{\eta_0 E_a/E_c + H_a/E_c} \right)^*.
\]

\(T = \frac{4\eta_0 \text{Re}(\eta_3)}{(\eta_0 E_a/E_c + H_a/E_c) (\eta_0 E_a/E_c + H_a/E_c)^*}.
\]

3. Results and discussion

3.1. The optical reflectance and transmittance of graphene and graphene-oxide on various substrates

The optical reflectance and transmittance are affected by the optical constants, the thickness of each layer, and the angle and wavelength of the incident light. Figure 2(a) shows the calculated reflectance of graphene-oxide as a function of the wavelength of the incident light (range: \(\lambda\): 380–780 nm) and of the graphene-oxide thickness \((d_1)\) on a 270 nm-thick SiO\(_2\) layer on a silicon substrate. The light was assumed to be normally incident to the surface. To express the optical properties of the graphene-oxide layer, we used a complex refractive index \((N_1 = n_1 + k_1 i)\). For the wavelength dependence of the optical properties, the index of refraction \((n_1)\) and the extinction coefficient \((k_1)\) were expressed by the Cauchy function described as \(n_1(\lambda) = A_n + B_n/\lambda^2\) and \(k_1(\lambda) = A_k + B_k/\lambda^2\) where \(A_n, A_k, B_n, \) and \(B_k\) are given coefficients; for non-reduced graphene-oxide, these coefficients are 1.7, 0.17, 3000, and 1500 for \(A_n, A_k, B_n, \) and \(B_k\), respectively [26].

The reflectance of graphene-oxide varies depending on the wavelength of the incident light and the material thickness as shown in figure 2(a). For the thickness region near 0 nm, the minimum reflectance \((R_{\text{min}})\) appears near the wavelength of 530 nm and the maximum reflectance \((R_{\text{max}})\) appears near the shortest given wavelength (∼380 nm). As the thickness increases, the wavelength for the minimum (or maximum) reflectance also increases. The ratio between the maximum and the minimum reflectances \((R_{\text{max}}/R_{\text{min}})\) is 5.1 for the thickness region near 0 nm and becomes as high as 11.5 near a thickness of 300 nm, indicating that the interference effect is active over the range of material thicknesses.

Figure 2(b) shows the reflectance of graphene deposited on the same substrate. For graphene, the coefficients of the Cauchy function are 2.0, 1.1, 3000, and 1500 for \(A_n, A_k, B_n, \) and \(B_k\), respectively [23]. In contrast to the graphene-oxide, the variation in the reflectance of graphene reduces substantially as the material thickness increases. For a thickness of 50 nm, the \(R_{\text{max}}/R_{\text{min}}\) is 2.2. This value reduces...
Figure 2. (a) Calculated reflectance as a function of the wavelength of incident light ($\lambda$) and the material thickness of graphene-oxide deposited on a 270 nm-thick SiO$_2$/Si layer. (b) Reflectance of graphene deposited on a 270 nm-thick SiO$_2$/Si layer. (c) Reflectance of graphene-oxide deposited on a 270 nm-thick SiO$_2$/air layer. (d) Reflectance of graphene deposited on a 270 nm-thick SiO$_2$/air layer. (e) Transmittance of graphene-oxide deposited on a 270 nm-thick SiO$_2$/air layer. (f) Transmittance of graphene deposited on a 270 nm-thick SiO$_2$/air layer.

3.2. Calculation of the colors of graphene and graphene-oxide on various substrates

To calculate the colors of the graphene and graphene-oxide multilayers, RGB parameters were determined by the suggested procedure [22]. In this procedure, RGB parameters were transformed from XYZ parameters, which were obtained by multiplying the reflectance (or transmittance) with the CIE color-matching functions ($X_\lambda$, $Y_\lambda$, $Z_\lambda$), and then integrating over the wavelengths such that $X = \int_0^\infty R P_i X_\lambda \, d\lambda$, $Y = \int_0^\infty R P_i Y_\lambda \, d\lambda$, and $Z = \int_0^\infty R P_i Z_\lambda \, d\lambda$, where $P_i$ is the intensity of the incident light, and $I$ is the illumination level. Note that the incident light intensity is a function of the wavelength. Additionally, the spectrum of a standard fluorescent light bulb was used to provide the wavelength dependence of the light source [22]. This spectrum enabled us to convert the XYZ parameters into RGB parameters via multiplication with the transformation matrix ($M$): $[R G B] = [X\ Y\ Z][M]^{-1}$. Further details about this transformation can be found in [22]. By following the procedure above, the reflectance and transmittance given in figure 2 can be
Figure 3. (a) Two-dimensional color image calculated as a function of the illumination level ($I$) and the thickness of graphene-oxide deposited on a 270 nm-thick SiO$_2$/Si layer. (b) Color image of graphene deposited on a 270 nm-thick SiO$_2$/Si layer. (c) Color image of graphene-oxide deposited on a 270 nm-thick SiO$_2$/air layer. (d) Color image of graphene deposited on a 270 nm-thick SiO$_2$/air layer. (e) Color image of graphene-oxide on a 270 nm-thick SiO$_2$/air layer (viewed from the side opposite the light source). (f) Color image of graphene deposited on a 270 nm-thick SiO$_2$/air layer (viewed from the side opposite the light source).

visualized by the colors shown in figure 3. The colors are presented as two-dimensional images with the change in the material thickness along the $x$-axis and the illumination level ($I$) along the $y$-axis.

Figure 3(a) shows the color image of the graphene-oxide multilayer on a 270 nm-thick SiO$_2$/Si substrate. The colors of the graphene-oxide multilayer vary with a loosely repeating pattern as the material thickness increases. Figure 3(b) shows the color image of the graphene multilayer on the same substrate. Compared to the graphene-oxide multilayer, the colors of the graphene multilayer show a simple, gradual transition from the color of the substrate to the saturated color as the thickness approaches 100 nm, which is likely a response to the high extinction coefficient of the graphene
Figure 4. (a) Three-dimensional representation of the angular distribution of light intensity from a lens, which follows a Gaussian distribution. (b) Weighting factors for the lens with a numerical aperture (NA) of 0.9, obtained by integrating the Gaussian distribution in the angular $\psi$ direction from (a). (c) Low-magnification optical microscope image of graphene-oxide film deposited on a 270 nm-thick SiO$_2$/Si substrate, where the height profile was measured from the red dashed line, the NA of the lens was 0.05, and the white scale bar for the upper part of the image represents 1 mm. The color chart in the lower part of the image indicates the graphene-oxide thickness. (d) High-magnification optical microscope image of an exfoliated graphite flake on the same substrate, where the NA of the lens was 0.9 and the white scale bar in the upper part of the image represents 25 $\mu$m. The color chart in the lower part of the image represents the graphene thickness.

3.3. Comparison between the calculated colors and the measured colors from optical microscopes

To be able to compare the calculated colors with the measured colors by optical microscopy, uncertainties—such as the total intensity and spectrum of the light source, the angle of incidence, and the sensitivity of the RGB detectors in the image acquisition system—must be resolved [22]. For example, the effect of the angle of incidence can be approximated by assuming that the light intensity from the lens follows a Gaussian distribution [18, 23]. Figure 4(a) shows a three-dimensional rendering of a Gaussian distribution of light intensity, where the dashed line indicates the maximum angle of light ($\theta_b$) that can exit the lens. This angle is determined by the numerical aperture (NA) of the lens using the relation $\theta_b = \sin^{-1}(NA)$. Then, the effect of the angular distribution of the incident light can be considered by averaging the reflectance multiplied by weighting factors ($\omega_\theta$) such that $\bar{R} = \sum R_\theta \omega_\theta$. Figure 4(b) shows the weighting factors as a function of the incident angle for a lens (NA = 0.9) obtained by integrating the surface of figure 4(a) in the angular ($\psi$) direction.

To experimentally observe the colors calculated above, we prepared a graphene-oxide multilayer by depositing graphene-oxide through a circular hole of a thin PDMS film [26]. The color image for the graphene-oxide multilayer deposited on a 270 nm-thick SiO$_2$/Si substrate is shown in figure 4(c). To create this image, an optical microscope (Bausch and Lomb microzoom microscope 2.25×, NA = 0.05, Panasonic WV-CP-244 camera) was connected to a probe station and a thickness profile was acquired from...
Figure 5. (a) Upper image: high-magnification optical microscope image of a graphene-oxide monolayer deposited on a 72 nm-thick Si$_3$N$_4$/Si layer; middle image: high-magnification optical microscope image of a few layers of graphene-oxide on the same substrate; lower image: calculated color chart of graphene-oxide as a function of layer number. The NA of the lens was 0.9, and all scale bars represent 25 µm. (b) Upper image: high-magnification optical microscope image of a graphene-oxide monolayer deposited on a 270 nm-thick SiO$_2$/Si layer; middle image: high-magnification optical microscope image of a few layers of graphene-oxide on the same substrate; lower image: calculated color chart of graphene-oxide as a function of layer number. As before, the NA of the lens was 0.9, and all scale bars represent 25 µm.

A profilometer (P-10; KLA Tencor, Inc.), which was then overlaid on top of the optical image. The color chart below the image was generated by optimizing the illumination level ($I$) in the calculation routine to match the measured colors of the substrates. The upper part of the image shows the color of the substrate while the lower section shows the color of the material as a function of the thickness. The colors from the optical microscopy and the relevant thicknesses from the profilometry are in good agreement with the theoretical calculations in the color chart.

Figure 4(d) shows a microscope image of the exfoliated graphene multilayer on a 270 nm-thick SiO$_2$/Si substrate. As before, this image was created using an optical microscope (Olympus PMG3 inverted metallurgical microscope with a high resolution (100×) lens, NA = 0.9, RTKE/SE digital camera with Spot Advanced 3.5.5). Note that the difference in the colors of the substrates is due to the difference in the numerical apertures of the lenses in each system, which are 0.05 and 0.9, respectively. The graphene multilayer has a maximum thickness of about 100 nm, as confirmed by atomic force microscopy (AFM). The calculated colors, represented by the color chart below the image, show good agreement with the observed colors of figure 4(d). (Note the various colors of the graphene multilayer in the dashed circle.)
3.4. The effect of dielectric layers on the colors and visibility of few-layer graphene-oxide

We further investigated the effects of both Si3N4 and SiO2 dielectric layers on the color and visibility of few-layer graphene-oxide. Figures 5(a) and (b) show the optical microscope images of few-layer graphene-oxide on 72 nm-thick Si3N4/Si and 270 nm-thick SiO2/Si layers, respectively. Here, we assumed that the thickness of the graphene-oxide monolayer was 1.25 nm according to that of previous reports [27, 28]. These images were obtained by the same optical system used in acquiring figure 4(d). As shown in that figure, the graphene-oxide on the surface of the Si3N4 layer exhibits stronger visibility than the SiO2 layer. This stronger visibility is likely a response to the low reflectance of the Si3N4 surface compared to that of the SiO2 surface. When the reflectance was averaged over the wavelength, which ranged from 380 to 780 nm, the averaged reflectance of the Si3N4 surface was 72% smaller than that of the SiO2 surface. Because the contrast is proportional to the change in reflectance divided by the reflectance of the substrate (ΔR/RSUBSTRATE), it is increased as the reflectance of the substrate becomes smaller [18]. More quantitatively, the visibility of graphene-oxide can be found by calculating the difference between the RGB parameters (ΔRGB, in %) of the substrate and the graphene-oxide layer:

\[
\Delta_{\text{RGB}} = (|R - R'| + |G - G'| + |B - B'|)/(R' + G' + B')
\]

(4)

where R, G, B are the RGB parameters of a graphene-oxide layer and R', G', B' are the values for the substrate. Consequently, the ΔRGB of the graphene-oxide monolayer was found to be approximately 1.9% on the SiO2 layer and 6.1% on the Si3N4 layer. Thus, the Si3N4 layer had a ΔRGB that was 3.2 times greater than that from the SiO2 layer. Similarly, for ten layers of graphene-oxide, we obtained ΔRGB values of 18.3% and 31.3% for the SiO2 and Si3N4 layers, respectively. Therefore, the graphene-oxide multilayer on a Si3N4 layer has a higher visibility than that on a SiO2 layer. The graphene multilayer, on the other hand, displayed no significant difference in ΔRGB values for the two substrate layers, which agrees with the previous report [23]. The measured images and calculated colors were well correlated, indicating that the number of layers can be estimated using color charts. In addition, we identified color charts for the graphene-oxide multilayer as a function of the thickness of the dielectric Si3N4 layer. The color charts exhibited diverse colors from yellow to blue corresponding to thicknesses ranging from 45 to 90 nm.

4. Conclusion

We studied the optical reflectance and transmittance of graphene and graphene-oxide multilayers deposited on various substrates and calculated the relevant colors by the color calculation routine. Since graphene-oxide has a lower extinction coefficient value than graphene, the reflectance of graphene-oxide more clearly fluctuates over a wide range of material thicknesses. Thus, the resulting colors of graphene-oxide repeatedly changed as a function of the material thickness, but the colors of the graphene multilayer became saturated without such periodic repetition. We experimentally confirmed the calculated colors of graphene-oxide by optical microscopy and profilometry. Consequently, color can potentially be employed as a tool for easy detection and simple evaluation of the thicknesses of graphene and graphene-oxide multilayer systems.

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