

Optical Properties of Multilayer Graphene

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[Summary]

Multilayer graphene is a promising candidate for optical device applications because its excellent optical properties can be controlled by the number of layers. This study measured the optical contrast, reflectance, and Raman scattering of multilayer graphene ranging in thickness from monolayer up to 107 nm, and comprehensively evaluated the optical properties, including correlations between these characteristics. The relationship between the number of graphene layers and color, which had previously only been understood qualitatively, was quantified for the first time by optical contrast, and demonstrated that the thickness can be determined from the contrast with an accuracy of ± 1 nm for thicknesses up to approximately 40 nm. We also demonstrated that the reflectance can be explained by the Fresnel equations by treating multilayer graphene as a uniform medium that ignores its layered structure. In addition to multiple reflections of the Raman scattered light, Raman spectroscopy showed the added importance of interference effects. Relationships between each of the characteristics were clarified by performing these measurements on the same sample.

1 Introduction

Graphene is a sheet-like material one carbon atom thick, possessing various outstanding physical properties, and is expected to find applications across a wide range of fields. Thanks to its atomic-scale thinness combined with excellent electrical and thermal conductivity, and that it can be exposed to the external environment, monolayer graphene is anticipated for use in applications such as electronic devices and molecular sensors. On the other hand, interlayer interactions when stacking graphene in multiple layers can enhance its original properties or give rise to entirely new ones, so applied research into multilayer graphene is also advancing. Of particular interest among these applications is its use in optical devices. Monolayer graphene exhibits a remarkably high absorbance of 2.3%, independent of wavelength¹⁾, and this absorbance can be controlled by varying the number of layers or the stacking structure^{2),3)} which has led to advanced research into applications such as antennas for electromagnetic fields and light.

Practical use of multilayer graphene requires knowing the number of layers (thickness) precisely. The thickness of a single graphene layer is approximately 0.334 nm, and accurate measurement uses instruments such as atomic force microscopes (AFMs) and scanning tunneling microscopes (STMs). However, while these instruments offer high resolution, considerable time is required to perform measurements. There is a simpler method for determining thickness that makes use of the “color” of graphene. On its own, graphene is transparent, but it can be “seen” under an optical microscope⁴⁾ by placing it on a Si substrate with a thermally grown oxide (SiO_2) film of appropriate thickness. By using the contrast relative to the substrate extracted as RGB or grayscale intensities from optical microscope images, it is possible to distinguish differences in thickness down to a single atomic layer for up to approximately six layers⁵⁾. The fact that the number of layers can be identified easily without using expensive instruments such as AFM may be regarded as one of the factors behind the explosive spread of graphene research and its applications.

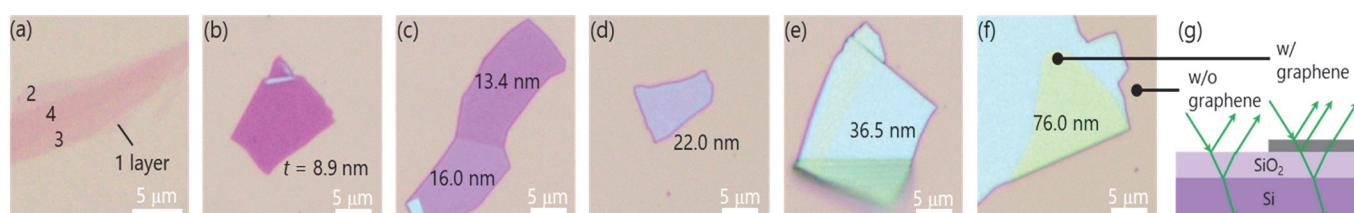


Figure 1 (a) to (f) Optical images of multilayer graphene of various thicknesses¹⁰⁾.

Numbers in figures indicate (a) number of graphene layers; (b)–(f) thickness measured by AFM.

(g) Schematic diagram showing difference in optical path of light incident on substrate with and without graphene.

On the other hand, the change in the color of graphene at thicknesses exceeding about ten layers remains understood only qualitatively. Specifically, on a Si substrate with the widely used 300-nm-thick SiO₂ surface layer, the color of graphene changes from reddish tones to bluish tones as the thickness increases, and eventually to metallic gray, the color of graphite. Thus, the fact that monolayer graphene, whose thickness is only 0.334 nm, can be observed under an optical microscope and moreover exhibits various colors depending on its thickness is not only practically useful for layer-number determination, but is also intrinsically fascinating.

According to reflectance spectrum measurements that yield a more fundamental physical quantity than RGB intensities, the spectra up to nine layers are accounted for by the Fresnel equations, and the number of layers can be determined from the reflectance at a wavelength of approximately 550 nm⁶⁾. In addition, Raman spectroscopy is also a known method for determining the number of layers by making use of the optical properties of graphene. In the very thin regime of approximately one to three layers, the number of layers can be determined with good accuracy from the intensity ratio of the 2D band, which arises from a second-order lattice vibrational process, to the G-band, which originates from in-plane vibrations of the carbon atom honeycomb lattice, as they appear in the Raman scattering spectrum. However, this method for determining the number of layers is not well suited to thicker regimes. The layer-number dependence of the G-band intensity has been investigated up to a thickness of about 30 nm (about 90 layers)⁷⁻⁹⁾, and it is known that the intensity first increases with thickness, then turns to decrease, and ultimately converges to a constant value. However, the thickness at which the intensity transitions from increasing to decreasing differs among research groups and has yet to be quantified.

While the layer-number dependence of optical properties such as RGB contrast, reflectance, and Raman scattering of graphene has been investigated, much of this understanding remains at a qualitative level, and each study has been carried out independently by different research groups. Consequently, there is still no unified understanding that includes the correlations between these individual properties. We therefore measured RGB intensities, reflectance, and Raman scattering spectra on the same samples of multilayer

graphene ranging in thickness from monolayer up to 107 nm (approx. 319 layers), along with an investigation of the relationship between thickness and color. This enabled direct comparison of the thickness dependence of each property, permitting a comprehensive study that also encompasses the relationships between them¹⁰⁾. This article presents the findings of this work.

This study used graphene prepared by exfoliating graphite onto a Si substrate with a 268-nm-thick SiO₂ surface layer. The thickness of the SiO₂ was determined from reflectance spectra as described later. The thickness (t) of the graphene was determined by AFM (Dimension XR, Bruker) measurements. The imaging conditions of optical microscopy (BX53M, Olympus Corporation) such as exposure time and aperture were fixed across all measurements unless otherwise noted. A spectroscopic reflectometer (TohoSpec3100, Toho Technology Corporation) was used for reflectance measurements. A laser Raman microscope (inVia Raman microscope, Renishaw plc) with an excitation wavelength of 532 nm was used for Raman spectroscopy. This article is structured as follows: Section 1 overviews the intriguing fact that graphene, a material of atomic-scale thinness, can be observed under an optical microscope, along with the current state of understanding regarding the layer-number dependence of the optical properties of graphene. Section 2 presents our research into the optical properties of multilayer graphene. Section 2.1 shows the results for RGB contrast, Section 2.2 for reflectance, and Section 2.3 for Raman scattering measurements, while Section 2.4 discusses the relationships between these properties.

2 Optical Properties of Multilayer Graphene

2.1 RGB Contrast

As illustrated by the optical images in Figures 1(a)–(f), graphene displays a rich variety of colors depending on its thickness. This is explained, as described later, by the reflection of light at each interface shown in Figure 1(g) and the resulting interference effects¹⁰⁾. The numerical values in the figures represent the number of graphene layers in Figure 1(a), and the thickness measured by AFM in Figures 1(b)–(f). Figure 2(a) shows the 256-level RGB intensities ($X_{R,G,B}$) extracted from the optical image of the one-to-four-layer graphene in Figure 1(a) against the number of graphene layers. The inset shows a histogram of X_G . From the inset, it can be seen that X_G takes

discrete values corresponding to the number of graphene layers, demonstrating that single-atomic-layer resolution is achievable. As shown in Figure 2(a), $X_{R,G,B}$ varies linearly with the number of layers, demonstrating that the number of graphene layers can be determined from $X_{R,G,B}$.

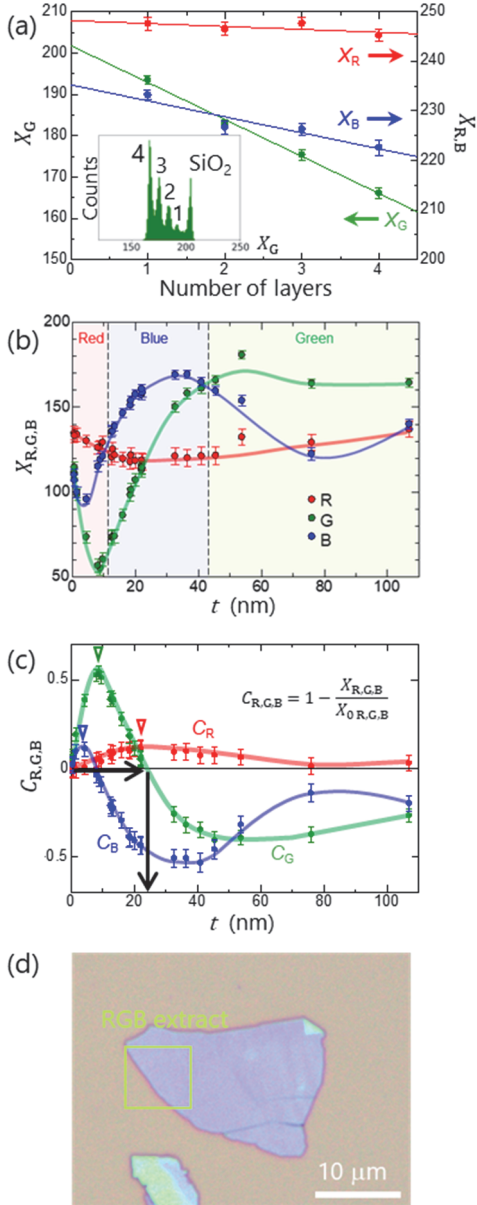


Figure 2 (a) RGB intensities $X_{R,G,B}$ of the one-to-four-layer graphene shown in Figure 1(a)¹⁰. The inset shows a histogram of X_G . (b) $X_{R,G,B}$ of multilayer graphene extracted from optical images¹⁰. (c) Optical contrast $C_{R,G,B}$ ¹⁰. (d) Optical image of multilayer graphene. $C_{R,G,B}$ was obtained from the region enclosed by the green frame, and the thickness was estimated from (c). Note that the $X_{R,G,B}$ values in Figure 2(a) were obtained from optical images acquired with a longer exposure time than the measurements described later in order to improve resolution in the very thin regime, and therefore the numerical values do not correspond to those in Figure 2(b).

Figure 2(b) shows $X_{R,G,B}$ plotted over the entire range of measured thickness t . As t increases, the dominant component shifts from red (X_R) to blue (X_B) at $t \sim 10$ nm, and then to green (X_G) at $t \sim 40$ nm. This study is the first to quantitatively evaluate the color changes of graphene, which had previously been understood only at a qualitative level.

The fact that graphene, an atomic-scale material, can be observed under an optical microscope and moreover displays a variety of colors depending on its thickness is explained by light interference effects. As shown schematically in Figure 1(g), incident light is reflected at each of the interfaces between air, graphene, SiO_2 , and Si, and these reflected lights are emitted externally. In practice, due to multiple reflections, there are countless optical paths of greater complexity than those depicted in the figure, and the light traveling along these paths interferes with one another. Whether the interference results in constructive or destructive superposition is determined by the ratio of the optical path difference to the wavelength. As a result, the intensity of the interfering light varies periodically with t , and this period becomes longer for light of longer wavelengths. In this way, since the t -dependence differs according to the wavelength of light, the color of graphene changes with increasing thickness.

However, there is individual variation of about ± 20 nm even among products with the same nominal SiO_2 thickness, and this variation changes the optical path length of light reflected at the SiO_2/Si interface, meaning that $X_{R,G,B}$ values differ from substrate to substrate even for graphene of the same thickness. While all data in Figure 2(b) were measured on the same substrate, the intensity ratio relative to the substrate—namely the contrast $C_{R,G,B}$ —is less susceptible to differences in SiO_2 thickness than the absolute values of $X_{R,G,B}$ and is therefore more practical as an index for the unified evaluation of graphene on different substrates.

In this study, the RGB contrast $C_{R,G,B}$ between graphene and the substrate was defined by the following equation:

$$C_{R,G,B} = 1 - \frac{X_{R,G,B}}{X_{0,R,G,B}}, \quad (1)$$

where $X_{R,G,B}$ is the RGB intensity of the graphene and $X_{0,R,G,B}$ is the RGB intensity of the substrate. Figure 2(c) shows the t -dependence of $C_{R,G,B}$ obtained from the $X_{R,G,B}$ values in Figure 2(b). It shows that $C_{R,G,B}$ increases with increasing t , but begins to decrease beyond a certain t , and the variation becomes small for $t > 40$ nm. The thickness at which $C_{R,G,B}$

transitions from increasing to decreasing is indicated by open triangles in Figure 2(c), and takes a different value for each color. This difference can be understood from the relationship between light interference and wavelength discussed earlier. That is, since the wavelengths of the RGB colors are ordered $B < G < R$ from shortest to longest, the maxima appear in the order $C_B < C_G < C_R$ from smaller to larger values of t .

Using Figure 2(c), we examined whether the layer-number determination method based on $C_{R,G,B}$ can be applied to regimes thicker than the six layers demonstrated in the prior study⁵⁾. Values of t can be determined uniquely by combining the values of C_R , C_G , and C_B extracted from optical images. Since the determination accuracy depends on the slope of the variation of $C_{R,G,B}$ with respect to t , it is effectively determined by C_G , which has the steepest slope. As a result, an accuracy of approximately ± 1 nm (roughly three atomic layers) can be achieved from this slope and the uncertainty in C_G up to about $t = 40$ nm. For example, the multilayer graphene shown in the frame in Figure 2(d) has $C_G = -0.01$, from which t is estimated to be 24 ± 1 nm. This value is in good agreement with the value measured by AFM of $t = 23.6$ nm.

2.2 Reflectance

As we have seen, $C_{R,G,B}$ is a very practical index that estimates layer number with high accuracy, despite being readily obtainable from an optical microscope. However, $C_{R,G,B}$ is not a direct physical quantity, because it represents the reflected light intensity multiplied by the spectral transmittance of the lenses and filters as well as the spectral sensitivity characteristics of the color sensor. It is also heavily dependent on the imaging conditions. Therefore, to evaluate the physical properties in detail, the t -dependence of the reflectance (R) across the visible light region was measured.

Figure 3(a) shows the R spectra of multilayer graphene ranging from monolayer up to $t = 107$ nm. The thick black line represents the R of the SiO_2/Si substrate. This figure shows that R varies substantially with wavelength particularly for thin graphene, but as the thickness increases this variation becomes smaller, ultimately converging to a value almost independent of wavelength.

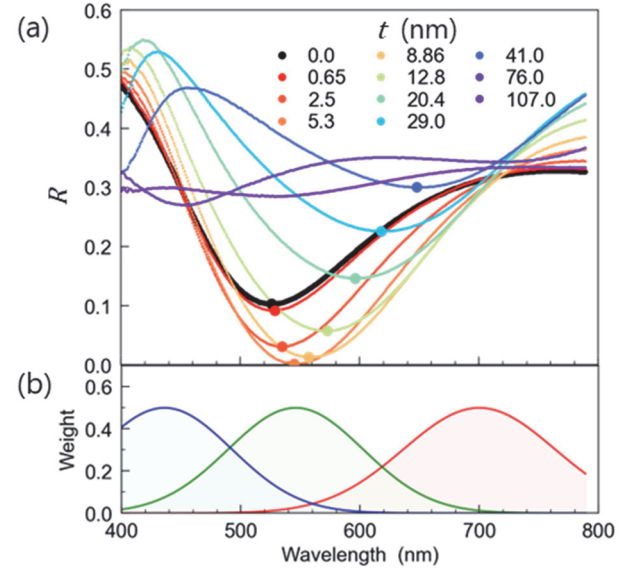


Figure 3 (a) Reflectance R of multilayer graphene of various thicknesses in the visible light region¹⁰⁾. Circles indicate local minimum values of R at each t . (b) Weighting functions for R, G, and B used in calculating virtual $X'_{R,G,B}$ from $R^{(0)}$.

As indicated by the circles in Figure 3(a) representing the local minimum values of R at each t , $R = 0$ at $t \sim 5$ nm and wavelength $\lambda \sim 550$ nm. This indicates that when monochromatic light of a specific wavelength ($\lambda \sim 550$ nm) is incident on graphene of a certain thickness ($t \sim 5$ nm), the graphene appears completely black and is effectively “invisible.” At this point, however, the contrast with the substrate is at its maximum, so graphene remains visible through its contrast with the substrate. In general, reflected light contains, in addition to light reflected at the material surface, components such as emitted light from each graphene layer including Raman scattered light¹¹⁾. However, this zero reflectance demonstrates that the influence of such emitted light components is negligibly small relative to the magnitude of R .

Next, virtual RGB intensities $X'_{R,G,B}$ were calculated from the experimentally obtained R , and compared with $X_{R,G,B}$ extracted from the optical images. Specifically, $X'_{R,G,B}$ were computed by integrating R over the wavelength range corresponding to each color, weighted by a Gaussian distribution as shown in Figure 3(b). The center wavelengths and full widths at half maximum (FWHM) of the Gaussian distributions in Figure 3(b) were set to 700 nm and 90 nm for R, 546.1 nm and 80 nm for G, and 435.8 nm and 80 nm for B. Note that, since the measured wavelength range of R is 400 to 800 nm, wavelength components outside this range are

discarded. Figure 4 shows $X_{R,G,B}$ and $X'_{R,G,B}$ calculated from R . Since the actual spectral sensitivity of each color sensor is more complex than a simple Gaussian distribution, the measured and calculated values do not agree perfectly. However, it is clear that $X_{R,G,B}$ is qualitatively reproduced by $X'_{R,G,B}$.

Subsequently, the experimentally obtained R was compared with theoretical calculations based on the Fresnel equations. For simplicity, as shown in Figure 5(a), we used a model in which multilayer graphene is assumed to be a homogeneous medium, ignoring its layered structure, and R was calculated from the following equations.

$$R = \frac{[r_1 e^{i(\varphi_1 + \varphi_2)} + r_2 e^{-i(\varphi_1 - \varphi_2)} + r_3 e^{-i(\varphi_1 + \varphi_2)} + r_1 r_2 r_3 e^{i(\varphi_1 - \varphi_2)}]^2}{e^{i(\varphi_1 + \varphi_2)} + r_1 r_2 e^{-i(\varphi_1 - \varphi_2)} + r_2 r_3 e^{-i(\varphi_1 + \varphi_2)} + r_1 r_3 e^{i(\varphi_1 - \varphi_2)}} \quad (2)$$

$$r_1 = \frac{n_0 - n_1}{n_0 + n_1}, \quad r_2 = \frac{n_1 - n_2}{n_1 + n_2}, \quad r_3 = \frac{n_2 - n_3}{n_2 + n_3} \quad (3)$$

$$\varphi_1 = \frac{2\pi n_1 t}{\lambda}, \quad \varphi_2 = \frac{2\pi n_2 d_{\text{SiO}_2}}{\lambda}, \quad (4)$$

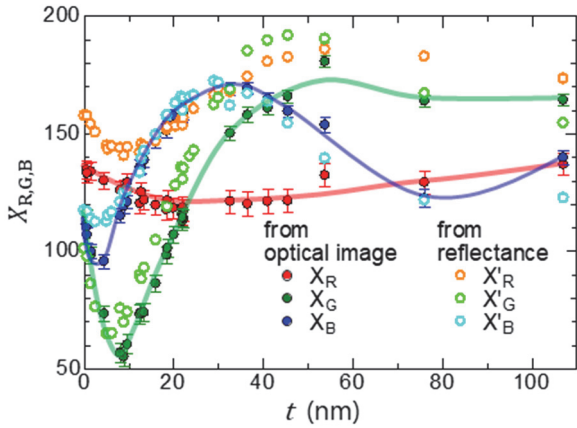


Figure 4 Comparison between $X_{R,G,B}$ extracted from optical images and $X'_{R,G,B}$ calculated from reflectance $R^{(0)}$. Solid lines are guides for the eyes.

Here, n_i ($i = 0, 1, 2, 3$) are the complex refractive indices of air, graphene, SiO_2 , and Si, respectively, λ is the wavelength of light, and d_{SiO_2} is the thickness of SiO_2 . In this calculation, the refractive index of air was set to $n_0 = 1$, the refractive index of multilayer graphene n_1 was taken from the literature value for monolayer graphene¹²⁾, and the refractive indices of SiO_2 and Si, n_2 and n_3 , were taken from literature values^{13),14)}. n_1 , n_2 , and n_3 are wavelength-dependent and cannot be expressed by simple formulas. For reference, $n_1 = 2.64 - 1.38i$, $n_2 = 1.46$, and $n_3 = 4.07 - 0.03i$ at $\lambda = 550$ nm. d_{SiO_2} was determined to be 268 ± 1 nm by fitting the

experimentally measured R of the SiO_2/Si substrate shown in Figure 5(b).

Figures 5(c)–(f) compare the experimentally measured R and the theoretical calculations based on the Fresnel equations for multilayer graphene of representative thicknesses. The measured values and calculated results are in very good agreement across the entire range of measured thicknesses and wavelengths. These results indicate that, for the R in the visible light region, multilayer graphene can be treated as a homogeneous medium with the layered structure ignored, and that evaluation of multilayer graphene using the refractive index of monolayer graphene remains valid for thicknesses up to 107 nm. This is also consistent with the result that the influence of emitted light, such as Raman scattering, on R can be ignored.

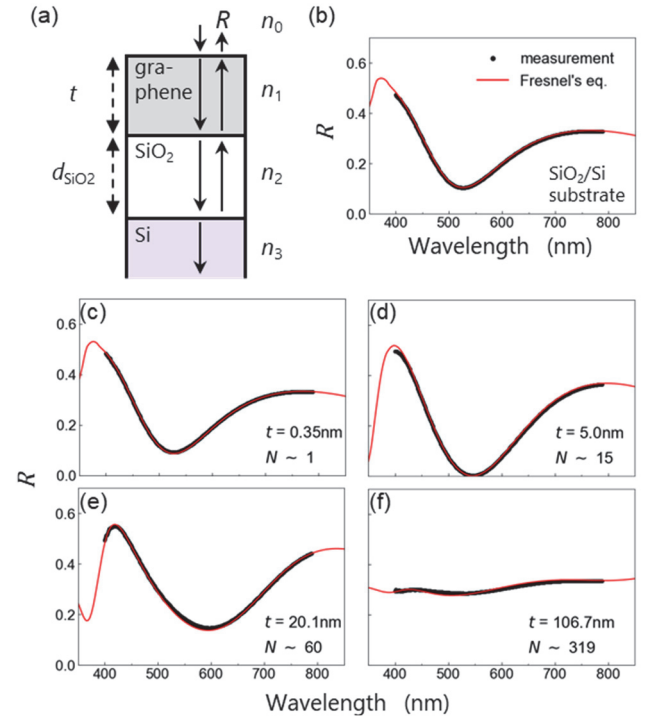


Figure 5 (a) Schematic diagram of model used for theoretical calculation of reflectance R . Comparison between experimentally measured R and calculated results based on Fresnel's equations for (b) SiO_2/Si substrate and (c)–(f) multilayer graphene of various thicknesses¹⁰⁾. Black circles are experimentally measured values obtained at a wavelength resolution of 1 nm, and red lines are calculated values.

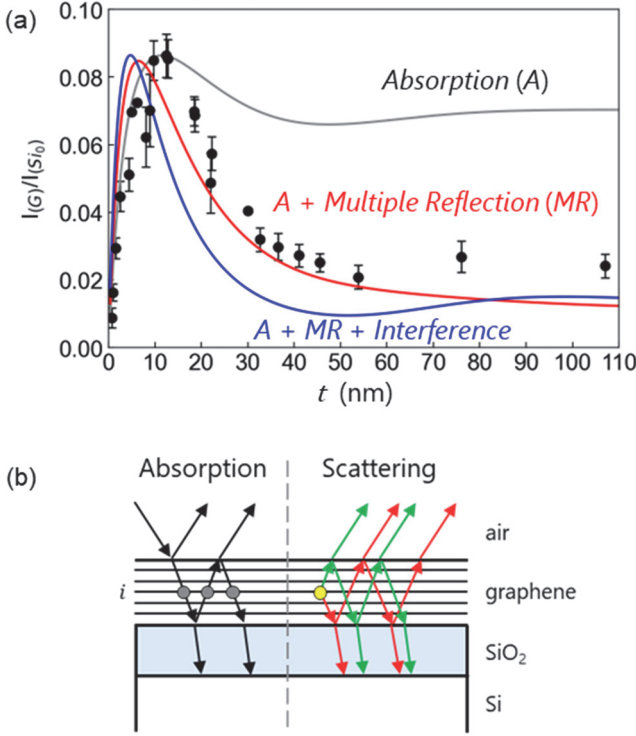


Figure 6 (a) Graphene thickness t dependence of G-band intensity ratio I_G/I_{Si0} ¹⁰. Black circles represent measured values, and solid lines show theoretical calculation results normalized in height direction. The gray line shows the result considering only graphene Absorption (A); the red line adds Multiple Reflection (MR) of the Raman scattered light to that; and the blue line further adds Interference of the Raman scattered light. (b) Schematic diagram of optical paths for light absorbed (left side of dashed line) and scattered (right side of dashed line) in graphene.

2.3 Raman Scattering Intensity

So far, we have focused on the reflected light component of the incident light on graphene, but there are also transmitted light and components absorbed by each graphene layer. A portion of the absorbed light is emitted as Raman scattered light. In this section, we evaluated the light absorption by multilayer graphene using Raman spectroscopy measurements. Among three major peaks known in the Raman scattering spectrum of graphene, namely the D, G, and 2D bands in order of increasing wavenumber, we focused on the layer number dependence of the G-band intensity (I_G), because its peak structure does not change with the number of layers. In Raman spectroscopy measurements, variation in signal intensity arises due to fluctuations in laser output between measurements. For this reason, each measurement was carried out by mapping a region containing both the graphene flake and the

SiO₂ surface, and evaluated using the intensity (I_G/I_{Si0}) normalized by the scattering peak intensity (I_{Si0}) originating from the Si beneath the SiO₂, as measured at the SiO₂ surface.

Figure 6(a) shows the dependence of I_G/I_{Si0} on t . As t increases, I_G/I_{Si0} increases with thickness up to $t \sim 12$ nm, but beyond that it begins to decrease, eventually settling at an approximately constant value. This behavior has been reported in previous studies⁷⁻⁹), but by extending measurements to even thicker regions, this study found that at around $t \sim 30$ nm the intensity does not simply converge monotonically to a constant value, but instead undergoes slight fluctuations.

To understand this behavior, we compared experimental results and theoretical calculations based on several models. First, the t -dependence of the Absorption (A) derived from the Fresnel equations was calculated. On the left side of the dashed line in Figure 6(b), the path of incident light into graphene is illustrated by black arrows. A portion of the incident light passes through the graphene multiple times while being partially reflected at each interface, and a portion of the light is absorbed by each graphene layer each time. In the figure, the absorption in the i -th layer counted from the top is indicated by gray circles. The total amount of light absorbed by graphene is calculated as the sum of the absorption in each i -th layer expressed as:

$$A = \sum_{i=1}^N |a_i|^2 \quad (5)$$

$$a_i = \frac{t_1 (e^{-2\pi k_1 z_i / \lambda_0} e^{-i2\pi n_1 z_i / \lambda_0} + r' e^{-2\pi k_1 z'_i / \lambda_0} e^{-i2\pi n_1 z'_i / \lambda_0})}{1 + r_1 r' e^{-i4\pi n_1 t / \lambda_0} e^{-4\pi k_1 t / \lambda_0}} \quad (6)$$

$$t_1 = \frac{2n_0}{n_0 + n_1} \quad (7)$$

$$r' = \frac{r_2 + r_3 e^{-i2\varphi_2}}{1 + r_2 r_3 e^{-i2\varphi_2}} \quad (8)$$

Here, N is the number of graphene layers, k_1 is the extinction coefficient of graphene (the imaginary part of the complex refractive index), $\lambda_0 = 532$ nm is the wavelength of the incident light, $z_i = 0.334 i$ (nm) is the depth of the i -th layer from the surface, and $z'_i = 2t - z_i$. The calculation result of Eq. (5) is shown as the gray line (A) in Figure 6(a). While the behavior of I_G/I_{Si0} increasing with t in the thin region is reproduced, for $t > 12$ nm, I_G/I_{Si0} decreases whereas A remains nearly constant, indicating that absorption alone is not sufficient to explain the results.

Therefore, a model that includes the Raman scattered light was considered. The right side of the dashed line in Figure 6(b) shows the path of Raman scattered light emitted from a given graphene layer. When Raman scattered light is emitted from the yellow circle in the figure, there is both a component directed outward (up in figure), shown by the green arrows, as well as a component directed toward the substrate side (down in figure), shown by the red arrows. Since these light components undergo repeated multiple reflections at each interface, there are countless complex paths, but only components that are ultimately emitted outward from the graphene surface are detected by Raman spectroscopy. Since not all the light scattered in this way is detected, the experimental values converge to a value smaller than $A^{15)}$. When multiple reflections of the Raman scattered light are considered, the G-band intensity can be expressed by the following equations, where b_i denotes the fraction of Raman scattered light emitted from the i -th layer counted from the top that is released to the outside¹⁵⁾.

$$I_G \propto \sum_{i=1}^N |a_i b_i|^2 \quad (9)$$

$$b_i = \frac{t'_1 (e^{-2\pi k_1 z_i / \lambda'} + r'_1 e^{-2\pi k_1 z'_i / \lambda'})}{1 + r'_1 r'_1 e^{-2\pi k_1 t / \lambda'}} \quad (10)$$

$$t'_0 = \frac{2n_1}{n_0 - n_1} \quad (11)$$

Here, λ' is the wavelength of the G-band Raman scattered light corresponding to the excitation wavelength of 532 nm, and is approximately 580.8 nm. This model assumes that the Raman scattered light is emitted with independent phases and that no interference occurs. Accordingly, Eq. (10) uses k_1 alone rather than the complex refractive index n_1 and excludes the phase term. The calculation result of Eq. (9) is shown as the red line ($A+MR$) in Figure 6(a). The behavior of I_G/I_{Si0} transitioning from increasing to decreasing is reproduced by considering the multiple reflections of the Raman scattered light, but the fluctuation of I_G/I_{Si0} observed at $t > 30$ nm is not reproduced. This is attributed to the assumption that interference between Raman scattered light that has traveled via different paths is neglected by using k_1 rather than n_1 in Eq. (10).

Therefore, a calculation incorporating the interference of Raman scattered light was performed. Specifically, k_1 in Eq. (10) was replaced by the complex refractive index n_1 , and the

G-band intensity was calculated from:

$$I_G \propto \sum_{i=1}^N |a_i b'_i|^2 \quad (12)$$

$$b'_i = \frac{t'_1 (e^{-2\pi n_1 z_i / \lambda'} + r'_1 e^{-2\pi n_1 z'_i / \lambda'})}{1 + r'_1 r'_1 e^{-2\pi n_1 t / \lambda'}} \quad (13)$$

This corresponds to considering only the interference between light that is scattered from the same graphene layer and emitted to the outside via different paths. The calculation result is shown as the blue line ($A+MR+Interference$) in Figure 6(a). Both the behavior of I_G/I_{Si0} transitioning to a decrease and the intensity fluctuations in the thicker region are reproduced. This result demonstrates that in order to understand Raman scattering in multilayer graphene, not only multiple reflections of the Raman scattered light but also interference effects are important.

Note that to focus on discussion of the thickness dependence, each calculation result in Figure 6(a) has been normalized so that the maximum values coincide. Further consideration is needed regarding absolute values of scattering intensity.

Finally, in the experimental results, the scatter in I_G/I_{Si0} becomes larger around $t = 10$ nm. A similar feature has been reported in several previous studies^{8),9)}, but the cause has not been clarified yet and is a subject for future investigation.

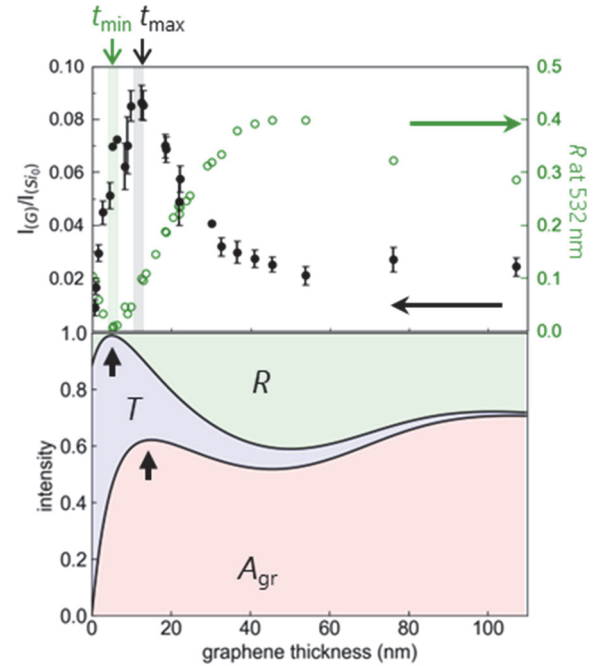


Figure 7 Top panel compares I_G/I_{Si0} and reflectance R at Raman excitation wavelength of 532 nm¹⁰⁾. Bottom panel shows fractions of reflectance R , transmittance T , and absorption in graphene A_{gr} relative to incident light, calculated by Fresnel's equations¹⁰⁾.

2.4 Comparison of Reflectance and Raman Scattering Intensity

Finally, we compared I_G/I_{SiO} , which corresponds quasi-equivalently to absorbed light, with reflectance R for reflected light at 532 nm—the same wavelength used in the Raman spectroscopy. The t -dependence of both quantities is shown in the top panel of Figure 7. As t increases, I_G/I_{SiO} first rises and then begins to decrease from $t_{\max} \sim 12$ nm, while R first decreases and then begins to increase from $t_{\min} \sim 5$ nm. Intuitively, it might be expected that when R is small, the amount of absorption increases and therefore I_G/I_{SiO} increases; but while the experimental values qualitatively follow this trend, the observed $t_{\min}$ and $t_{\max}$ are not equal. This is thought to be because not all the non-reflected light is absorbed by graphene. Instead, there is a component T that transmits through the graphene and penetrates into the SiO₂/Si substrate. The bottom panel of Figure 7 shows the t -dependence of the reflectance R , transmittance T , and the absorption into graphene A_{gr} obtained from $A_{gr} = 1 - R - T$ of multilayer graphene calculated using the Fresnel equations. T was calculated using the following equation.

$$T = \left[\frac{t_1 t_2 t_3}{e^{i(\varphi_1 + \varphi_2)} + r_1 r_2 e^{-i(\varphi_1 - \varphi_2)} + r_2 r_3 e^{-i(\varphi_1 + \varphi_2)} + r_1 r_3 e^{i(\varphi_1 - \varphi_2)}} \right]^2 \quad (14)$$

$$t_2 = \frac{2n_1}{n_1 + n_2}, \quad t_3 = \frac{2n_2}{n_2 + n_3} \quad (15)$$

Here, from Eqs. (7) and (15), the denominator of Eq. (14) is a constant, and since φ_1 is proportional to t from Eq. (4), T decreases approximately exponentially with respect to t . The presence of this component explains why the t value at which R reaches its minimum and the t value at which A_{gr} reaches its maximum are offset from each other. This offset is understood as the observed difference between $t_{\min}$ and $t_{\max}$.

3 Conclusions

Focusing on the fact that the color of multilayer graphene changes significantly with thickness, we measured the optical properties, including optical contrast, reflectance, and Raman scattering, of multilayer graphene ranging in thickness from monolayer up to 107 nm. Furthermore, we conducted a comprehensive study that also includes the correlations between each of these properties by performing these measurements on the same sample.

First, we quantitatively evaluated for the first time the change in color of multilayer graphene with thickness using the RGB contrast of optical images that had until now only been known qualitatively. We also demonstrated that the simple method of determining the number of graphene layers from RGB contrast remains valid with an accuracy of approximately ± 1 nm (three atomic layers) even for thick graphene up to $t \sim 40$ nm.

Second, we measured reflectance as a more fundamental physical quantity than RGB, and showed that the spectra can be almost completely reproduced by the Fresnel equations for thicknesses ranging from a monolayer up to 107 nm (about 319 atomic layers). This means that multilayer graphene can be treated as a uniform medium, ignoring its layered structure, from the perspective of reflectance. Furthermore, we demonstrated that the refractive index of monolayer graphene remains applicable up to a thickness of 107 nm and clarified that the reflectance of graphene of a specific thickness can reach zero for incident light of a specific wavelength. These results suggest that light emitted from each graphene layer, such as Raman scattered light, is negligible compared to the reflected light intensity.

Raman spectroscopy was performed to investigate light absorption by graphene. We observed for the first time that, in addition to the Raman scattering intensity first increasing and then transitioning to a decrease with increasing graphene thickness, the intensity also fluctuates at thicknesses of 30 nm and above. This indicates that not only multiple reflections but also interference effects are important for Raman scattering.

Lastly, we directly compared the thickness dependence of these optical properties and clarified the relationships between them. Although the thickness at which reflectance reaches its minimum does not match the thickness at which Raman scattering intensity reaches its maximum, this discrepancy can be understood by considering the respective contributions of reflection, transmission, and absorption.

This study demonstrated a practical method for determining the number of layers in multilayer graphene, while also clarifying its fundamental optical properties. These findings are expected to contribute to future applied research aimed at fabricating multilayer graphene optical devices.

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