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Thickness identification of two-dimensional materials by optical imaging

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Abstract
Two-dimensional materials, e.g. graphene and molybdenum disulfide (MoS₂), have attracted great interest in recent years. Identification of the thickness of two-dimensional materials will improve our understanding of their thickness-dependent properties, and also help with scientific research and applications. In this paper, we propose to use optical imaging as a simple, quantitative and universal way to identify the thickness of two-dimensional materials, i.e. mechanically exfoliated graphene, nitrogen-doped chemical vapor deposition grown graphene, graphene oxide and mechanically exfoliated MoS₂. The contrast value can easily be obtained by reading the red (R), green (G) and blue (B) values at each pixel of the optical images of the sample and substrate, and this value increases linearly with sample thickness, in agreement with our calculation based on the Fresnel equation. This method is fast, easily performed and no expensive equipment is needed, which will be an important factor for large-scale sample production. The identification of the thickness of two-dimensional materials will greatly help in fundamental research and future applications.

1. Introduction

Two-dimensional materials, e.g. graphene and its derivatives, graphene oxide (GO), hydrogenated graphene, nitrogen/boron-doped graphene, single- and few-layer boron nitride (BN) and molybdenum disulfide (MoS₂), have attracted great interest recently due to their intriguing electrical, mechanical, thermal and optical properties [1–8]. In order to investigate the properties of two-dimensional materials, one crucial step is to identify the thickness, which would strongly affect their electronic [9, 10], optical [11] and other properties.

Many methods have been used to identify the thickness of two-dimensional materials, e.g. atomic force microscopy (AFM) and high resolution transmission electron microscopy [12–14]. However, those methods need expensive equipment and are time consuming with slow throughput. Raman spectroscopy has been widely used to identify the thickness of graphene. The narrow (∼30 cm⁻¹) and symmetric 2D peak is characteristic of mechanically exfoliated (ME) one-layer graphene [12]. However, this method failed for a few layers of graphene grown by the chemical vapor deposition (CVD) method, which also presents a single Lorentzian 2D peak due to mis-oriented stacking.
geometry [15, 16]. The ratio of the intensity of the 2D peak to the G peak, denoted as $I_{2D}/I_G$, has been used to identify the thickness of CVD grown graphene [16]. Nevertheless, this method is invalid for doped graphene (with electrons/holes [17] and nitrogen/boron [18, 19]) and graphene with numbers of defects [20], as the intensity of the 2D peak is strongly dependent on doping and defects. The identification of the thickness of GO and MoS$_2$ is even more difficult, as the Raman features of these materials are not very sensitive to their thicknesses [14, 21]. White light contrast spectroscopy can be used to distinguish the layer number of ME graphene and GO [22, 23], it can also be used to identify the thickness of CVD grown graphene with arbitrary stacking order [24, 25], as the stacking geometry has little effect on the reflective index of two-dimensional materials. However, a continual white light source, spectrometer and expensive charged coupled device (CCD) detector are also required [22, 23].

In this paper, optical imaging is used as a simple and universal method to identify the thickness of two-dimensional materials. It is found that contrast values of graphene obtained from the green (G) channel image and those of MoS$_2$ obtained from the red (R) channel image are dependent on the numbers of layers. By obtaining the contrast values, the thickness of two-dimensional materials, i.e. graphene (ME and nitrogen-doped), GO and MoS$_2$ can be determined.

2. Experimental details

ME graphene and thin MoS$_2$ layers were fabricated by the mechanical exfoliation technique and transferred on a SiO$_2$/Si substrate. GO was synthesized following Hummers method [26]. Nitrogen-doped graphene samples were prepared by the CVD method and grown on copper foil using hydrogen and methane as gas sources. Ammonia gas was introduced during the reaction process to achieve nitrogen doping [27]. Raman spectroscopy and AFM were used to confirm the thickness of the samples. An Olympus BX51 microscope was used to obtain optical images of the samples and Matlab software was used to read the R, G, blue (B) values at each pixel of the optical images.

3. Results and discussion

CCD in optical microscope allows us to capture digital images of samples. The Bayer color filters in CCD divide incident light by R, G and B wavelength ranges. Given the phosphor used for the computer display and the fluorescent light used, the R, G and B values could reproduce a reflection spectrum from the surface of the sample [28]. The relative wavelength range with transmission larger than 20% of a commonly used Bayer RGB filter in a CCD is 435 nm–520 nm for the B filter, 520 nm–590 nm for the G filter and 590 nm–720 nm for the R filter, respectively.

The contrast spectrum $C(\lambda)$ of graphene samples on SiO$_2$(285 nm)/Si substrate can be calculated by the Fresnel equation under normal incident conditions [23]

$$C(\lambda) = \frac{R_0(\lambda) - R(\lambda)}{R_0(\lambda)}.$$  

Here, $R_0(\lambda) = |r_0(\lambda)|^2$ and $R(\lambda) = |r(\lambda)|^2$ are the reflected light intensities from the air/SiO$_2$ on Si and air/graphene/SiO$_2$/Si system, which are wavelength dependent.

$$r_0(\lambda) = \frac{r_{02} + r_{23}e^{-2i\phi_2}}{1 + r_{02}r_{23}e^{-2i\phi_2}}$$  

$$r(\lambda) = \frac{r_{01} + r_{01}r_{12}r_{23}e^{-2i\phi_2} + r_{12}e^{-2i\phi_1} + r_{23}e^{-2i(\phi_1+\phi_2)}}{1 + r_{12}r_{23}e^{-2i\phi_2} + r_{01}r_{12}e^{-2i\phi_1} + r_{01}r_{23}e^{-2i(\phi_1+\phi_2)}}.$$  

Under normal incidence, $r_j = \frac{n_j - n_0}{n_j + n_0} (i, j$ is taken from 0 to 3). $n_0, n_1, n_2$ and $n_3$ are the refractive indices of air, graphene, SiO$_2$ and Si, respectively. The consideration of the refractive index of the material as a function of wavelength (dispersion of light) is important and this dispersion must be included in the calculation. The refractive indices used in this calculation are obtained from [23, 29]. $\phi_{1,2} = \frac{2\pi n_i d_i}{\lambda}$ is the phase difference when light passes through SiO$_2$ or graphene layers. $d_2$ is the thickness of the SiO$_2$ layer. $d_1 = N \times d$ is the thickness of the graphene layers, where $N$ is the number of layers and $d = 0.335$ nm is the thickness of one-layer graphene [23].

Figure 1 gives theoretically calculated results of contrast spectra of graphene samples with different thicknesses (one, two, three, four, five, seven and nine layers) on SiO$_2$(285 nm)/Si substrate under normal incident light based on the Fresnel equation. The transmission ranges for R, G and B filters are also labeled. As can be seen from this figure, the contrast value increased as the number of layers increased, which makes unambiguous identification of the thickness of graphene possible (this is discussed in detail in our previous work [23]). We then calculated the integration of the contrast values in R, G and B transmission regions respectively.
The average contrast values of one-layer graphene for RGB transmission regions are 0.031 (R), 0.077 (G) and 0.0114 (B), individually, which are obtained by using the integrated value divided by the corresponding transmission range. The R, G and B transmission ranges used in this paper are 590 nm–720 nm (R), 520 nm–590 nm (G) and 435 nm–520 (B), following those of the Bayer RGB filter in the CCD. The theoretical contrast values for one to four layers of graphene are 0.077 (G), 0.149 (G), 0.216 (G) and 0.278 (G), respectively.

Figure 2(a) gives the optical image of one to four layers of graphene transferred on a SiO\(_2\) (285 nm)/Si substrate whose layer number is pre-identified by Raman/white light spectroscopy. Figures 2(b)–(d) display R, G and B channel images of the original optical image using a grayscale for easier viewing. From the R channel image in figure 2(b), it can be seen that contrast values of graphene samples vary with thickness, but the image is blurred. However, for figure 2(d), which shows the B value at each pixel, the whole image gives a similar gray level and it is hard to distinguish graphene samples and substrate. The contrast values of graphene samples are found to be much higher when displaying the G channel, as shown in figure 2(c). These results also match quite well with the theoretical calculation of the average contrast in the RGB range. The average contrast in the G range (0.077) is higher than that in the R range (0.031), and the average contrast in the B range is the lowest (0.011).

The contrast values obtained theoretically and experimentally from the G values for one to four layers of graphene are shown in figure 2(e). By uploading the digital image (figure 2(a)) on to a computer, 20 random points from the graphene sample and substrate are taken and the average and standard deviation of G values is obtained. The contrast value C is then calculated by the equation:

\[
C = \frac{G_{\text{sub}} - G_{\text{sam}}}{G_{\text{sub}}}. \tag{4}
\]

Here, \(G_{\text{sub}}\) is the G value taken from the substrate and \(G_{\text{sam}}\) is the G value taken from the graphene sample. C values for one to four layers of graphene are then obtained as 0.081, 0.171, 0.241 and 0.309, which can be fitted as:

\[
C = 0.0778x + 0.005. \tag{5}
\]

Here, \(x\) is the number of graphene layers, and for the substrate \(x\) is taken as 0. From this figure, it can be seen that the experimental values match quite well with the theoretical results. Figure 3 presents a three-dimensional contrast image of the G value of graphene samples. The G value at each pixel in the original optical image can be obtained by using the ‘imread’ function of the Matlab software. The contrast value at every pixel can be calculated by using equation (4) given in this paper and the contrast image can then be constructed as shown in figure 3. The optical image used for obtaining the contrast image is given in the lower-right corner from [23]. The contrast values for one to four layers of graphene are also labeled in this figure.

Jung et al proposed that the color of graphene can be used to identify its thickness [30]. As a comparison, ME graphene samples on SiO\(_2\) (300 nm)/Si substrate are exposed to a white light source with and without a white balance filter, and the optical images are shown in the corner of figures 4(a) and
on a SiO$_2$.

Figures 4(c) and (d) show the optical image and G channel thickness of nitrogen-doped CVD grown graphene and GO. An optical image is a more universally applicable method. The thickness of graphene, obtaining the contrast value from Raman spectroscopy. Compared with using color to identify the thicknesses of two-dimensional materials. However, the identification of the thickness of GO is always a difficult issue and here we provide a very simple method to solve it.

The thickness of one-layer graphene is shown in figure 4(e). The strong D and D′ peaks are due to large numbers of defects induced by nitrogen doping. As a result of strong doping and high density of defects, the I$_{2D}$/I$_G$ is only $\sim$1.15, which is much smaller than that of ME one-layer graphene (commonly larger than 3) [12].

On the other hand, the contrast of the G value of one-layer nitrogen-doped graphene is obtained from the optical image, which is 0.05, and matches very well with the calculated result. Therefore, optical imaging is a more general way of determining the thickness of doped graphene. Figures 4(f) and (g) show the optical image and R channel image of GO transferred on SiO$_2$(300 nm)/Si substrate whose thickness is further checked by white light contrast spectroscopy and AFM. It can be seen that the contrast of GO is much higher when displaying the R channel than that of the optical image. The contrast values for one to five layers of GO are 0.03, 0.07, 0.10, 0.13 and 0.16, respectively. This observation matches quite well with white light contrast measurements. The identification of the thickness of GO is always a difficult issue and here we provide a very simple method to solve it.

Table 1. Theoretical R, G and B values for one-layer graphene transferred on different substrates.

<table>
<thead>
<tr>
<th>Substrate used for transferring graphene</th>
<th>R</th>
<th>G</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ (100 nm, 200 nm, 285 nm, 300 nm, 400 nm)/Si</td>
<td>0.078</td>
<td>0.079</td>
<td>0.047</td>
</tr>
<tr>
<td>SiO$_2$ (100 nm, 200 nm, 285 nm, 300 nm, 400 nm)/Si</td>
<td>-0.004, -0.001, 0.027, -0.031, 0.077, 0.011, 0.049, 0.054, 0.002, 0.003, 0.005, 0.064</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$(72 nm)/Si [31]</td>
<td>0.023</td>
<td>0.052</td>
<td>0.119</td>
</tr>
<tr>
<td>Quartz</td>
<td>-0.052</td>
<td>-0.060</td>
<td>-0.070</td>
</tr>
<tr>
<td>PZT (lead zirconate titanate)</td>
<td>-0.011</td>
<td>-0.013</td>
<td>-0.015</td>
</tr>
<tr>
<td>Hexagonal-BN(14 nm)/SiO$_2$ (285 nm)/Si [32]</td>
<td>0.054</td>
<td>0.042</td>
<td>0.001</td>
</tr>
<tr>
<td>Hexagonal-BN crystal [32]</td>
<td>-0.026</td>
<td>-0.030</td>
<td>-0.035</td>
</tr>
</tbody>
</table>

(b). It can be seen that the color of graphene is dependent on the incident light source. Figures 4(a) and (b) give G channel images of ME graphene samples, and the contrasts of G values for one-layer graphene can be obtained, which are 0.05 and 0.05 for figures 4(a) and (b). This observation agrees very well with the calculated results, as shown in table 1. The thickness of one-layer graphene is checked by Raman spectroscopy. Compared with using color to identify the thickness of graphene, obtaining the contrast value from an optical image is a more universally applicable method.

Optical imaging can also be used to identify the thickness of nitrogen-doped CVD grown graphene and GO. Figures 4(c) and (d) show the optical image and G channel image of nitrogen-doped CVD grown graphene transferred on a SiO$_2$(300 nm)/Si substrate. The N/C atomic ratio for this sample is $\sim$3% as checked by x-ray photoelectron spectroscopy. The Raman spectrum of one-layer nitrogen-doped graphene is shown in figure 4(e). The strong D and D′ peaks are due to large numbers of defects induced by nitrogen doping. As a result of strong doping and high density of defects, the I$_{2D}$/I$_G$ is only $\sim$1.15, which is much smaller than that of ME one-layer graphene (commonly larger than 3) [12].

On the other hand, the contrast of the G value of one-layer nitrogen-doped graphene is obtained from the optical image, which is 0.05, and matches very well with the calculated result. Therefore, optical imaging is a more general way of determining the thickness of doped graphene. Figures 4(f) and (g) show the optical image and R channel image of GO transferred on SiO$_2$(300 nm)/Si substrate whose thickness is further checked by white light contrast spectroscopy and AFM. It can be seen that the contrast of GO is much higher when displaying the R channel than that of the optical image. The contrast values for one to five layers of GO are 0.03, 0.07, 0.10, 0.13 and 0.16, respectively. This observation matches quite well with white light contrast measurements. The identification of the thickness of GO is always a difficult issue and here we provide a very simple method to solve it.

Figures 5(a), (c) and (e) give optical images of one, two, three and five layers of MoS$_2$ transferred on SiO$_2$(300 nm)/Si substrate whose thicknesses are identified by Raman spectroscopy and AFM. Figures 5(b), (d) and (f) show R channel images of those optical images. Twenty random points from the sample and substrate are taken and the average contrasts of R values are obtained and shown in figure 5(g). It can be seen that the contrast of the R values linearly increases with increasing sample thickness, which makes the unambiguous identification of MoS$_2$ thickness possible. Raman spectroscopy has been proposed to distinguish the number of MoS$_2$ layers by monitoring the positions of E$_{2g}$ and A$_{1g}$ peaks. However, the frequency difference is only $\sim$1–3 cm$^{-1}$ for MoS$_2$ with different thicknesses, which makes this method not very accurate [14].

From the above examples, we find that optical imaging with RGB contrast is a universal method to distinguish the thicknesses of two-dimensional materials. However, the selection of G, R or B values should depend on the material and substrate used. For graphene transferred on a SiO$_2$(285 nm)/Si substrate, the average contrast in the G range is better than that in the R(B) range. Therefore, for graphene transferred on a SiO$_2$(285 nm)/Si substrate, obtaining the G value is the best way to identify the thickness
of graphene. Table 1 gives the theoretical results of average R, G and B values for commonly used transfer substrates for one-layer graphene [31, 32]. From this table, it can be seen that for different substrate we can select particular channels among the RGB channels to identify the thickness of graphene and delete the effect of poor contrast channels. In this table, values less than zero mean that the intensity of the reflected light from graphene is higher than that from the substrate.

Optical imaging to identify the thickness of two-dimensional materials has been carried out by some other research groups. Roddaro et al proposed the idea that the reflection spectrum can be converted into RGB channels and the variation of graphene thickness can be monitored by R, G and B values [33]; however, they did not give the quantitative analysis. Bruna et al analyzed the thickness of graphene by using a monochromatic image [34], and a special light source was needed for their analysis. Gao et al and Chen et al used a color difference method based on a combination of reflection spectra and International Commission on Illumination (CIE) space to determine the thickness of graphene [35, 36]. Unlike their methods, we select a certain channel among the RGB channels which has the highest contrast, and this will increase the resolution of the contrast of the graphene samples. Besides, no complex calculation of color difference is needed. Li et al used R values to identify one to three layer of MoS$_2$; however, they also did not give the quantitative analysis in the contrast value [37].

4. Conclusions

In summary, we have demonstrated that the contrast value of a two-dimensional material can be used to identify its thickness. The contrast value can be easily obtained by reading the R, G and B values at each pixel of the optical images of the sample and substrate, and this value linearly increases with increasing thickness of the sample, with G values working best for graphene on a SiO$_2$(285 nm)/Si substrate and R values working best for MoS$_2$ on a SiO$_2$(300 nm)/Si substrate. The thicknesses of GO and nitrogen-doped graphene are further checked for demonstration. We also suggest the selection of an RGB channel for graphene to identify its thickness when transferred on different substrates. This method is fast, easily performed and no expensive equipment is needed, which will be important for large-scale sample production. Identification of the thickness of two-dimensional materials will greatly help in fundamental research and future applications.

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