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Optical contrast determination of the thickness of SiO_2 film on Si substrate partially covered by two-dimensional crystal flakes

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Abstract SiO_2/Si substrate has been widely used to support two-dimensional (2-D) crystal flakes grown by chemical vapor deposition or prepared by micromechanical cleavage. The visibility of 2-D flakes is very sensitive to the thickness of the SiO_2 layer (h_{SiO_2}), which can not be determined precisely after the deposit of 2-D flakes. Here, we demonstrated a simple, fast and nondestructive technique to precisely determine h_{SiO_2} of SiO_2 films on Si substrate only by optical contrast measurement with a typical micro-Raman confocal system. Because of its small lateral resolution down to the micrometer scale, this technique can be used to access h_{SiO_2} on SiO_2/Si substrate that has been partially covered by 2-D crystal flakes, and then further determine the layer number of the 2-D crystal flakes. This technique can be extended to other dielectric multilayer substrates and the layer-number determination of 2-D crystal flakes on those substrates.

Keywords Dielectric substrate · Thickness · 2-D crystal flakes · Optical contrast · Numerical aperture

1 Introduction

Since graphene was first obtained by micromechanical cleavage from natural graphite [1], more and more atomically thin two-dimensional (2-D) crystals have been found, such as BN, MoS_2, GaSe, and so on, attracting emerging interest due to potentially interesting physical properties. The graphene flakes are usually deposited on the Si wafer covered by a SiO_2 film. The thickness of the SiO_2 film is chosen to make graphene flakes visible in the optical microscope by means of optical interference within the air/flake/SiO_2/Si multilayer. For the purpose of device application, graphene flakes are usually deposited on the substrate with SiO_2 thickness (h_{SiO_2}) of about 300 nm, which can bear a large breakdown voltage for the device [2, 3]. To get the maximum Raman intensity of graphene flakes, h_{SiO_2} of the substrate is usually chosen to be about 90 nm. For the visibility of other 2-D materials, h_{SiO_2} can be different. For example, MoS_2 monolayers can be identified more easily if either 55 or 220 nm is chosen for the thickness of SiO_2, yielding an optical contrast (OC) of 60 % for 500 nm wavelength illumination [4]. Determination of the layer thickness of SiO_2 on Si substrate for supporting 2-D materials is crucial for their basic research and device development.

There are several techniques to access the thickness of SiO_2 films on Si substrate [5, 6], such as X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), transmission electron microscopy (TEM), multiple-beam interferometry [7] and step profiler [8]. Particularly, spectroscopic ellipsometer has been one of the most used techniques capable of giving accurate thickness measurements due to being both rapid and low cost [5]. However, these techniques usually require large and expensive instrumentations and large sample size. For as-prepared 2-D crystal flakes on SiO_2/Si substrate with unknown SiO_2-layer thickness, a simple, precise and microprobing technique down to micrometer is necessary to keep the 2-D crystal flakes nondestructive during the measurement process.

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In this paper, we demonstrated a simple, fast and non-destructive technique to determine the layer thickness of SiO_2 films on Si substrate. The technique is based on OC measurement by micro-optical system and can probe the SiO_2 films with lateral size down to several micrometer. Based on this technique, we determined the layer thickness of SiO_2 films on which graphene flakes were deposited by mechanical exfoliation and further determined the layer number of those graphene flakes, which was confirmed by Raman measurement. This technique can be extended to other dielectric multilayer substrate and the layer number of other 2-D crystal flakes on the substrate.

2 Experimental details

Optical contrast and Raman spectroscopy measurements were performed in a backscattering geometry at room temperature using a Jobin-Yvon HR800 micro-Raman system, which is equipped with liquid nitrogen-cooled charge-coupled device and three objectives of 100× ($\mathrm{NA} = 0.90$), 50× ($\mathrm{NA} = 0.55$) and 50× ($\mathrm{NA} = 0.45$). Tungsten halogen lamp was used as a light source for OC measurement. The excitation wavelength for Raman spectra is 633 nm from a He–Ne laser with the power <0.5 mW to avoid sample heating.

Graphene flakes were obtained by micromechanical cleavage of natural graphite on SiO_2/Si substrate. Several substrates with different thickness of SiO_2 film on Si (100) wafer were used in this study. The SiO_2 film was prepared by thermal oxidation method. The thickness of SiO_2 layer was precisely determined by a spectroscopic ellipsometer. A mirror (MM2-311-25) from Semrock company was used as a reference, which exhibits a high reflectivity up to 99 % in the range from 350 to 1,100 nm. The OC is defined as $\delta(\lambda) = 1 - R_{\mathrm{smp}}(\lambda)/R_{\mathrm{ref}}(\lambda)$, where $R_{\mathrm{smp}}(\lambda)$ and $R_{\mathrm{ref}}(\lambda)$ are the reflected light intensities from research target (sample) and reference, respectively, dependent on the wavelength (λ) of the light source. To get the OC of graphene flakes on SiO_2/Si substrate, $R_{\mathrm{smp}}(\lambda)$ and $R_{\mathrm{ref}}(\lambda)$ are the reflected light intensities from the SiO_2/Si substrate with and without graphene flakes covered.

3 Results and discussion

When light from a lamp source is incident into a dielectric multilayers containing air, few-layer graphenes (FLG) and SiO_2/Si substrate, the effect of multiple reflection interference at its interfaces and in its interlayers can make significant different OCs between FLG on SiO_2/Si substrate. This makes FLG visible on dielectric multilayer substrate. In principle, such effect also exists in the air/SiO_2/Si trilayer. We performed the OC measurements on the two Si substrates covered by 89- and 301-nm SiO_2 layers, respectively, where the thickness of SiO_2 layer was precisely determined by spectroscopic ellipsometer. A Semrock mirror (MM2-311-25) with 99 % reflectivity in the range 350–1,100 nm was taken as a reference. Micro-Raman confocal system and a 50× objective with a numerical aperture (NA) of 0.45 were used in the measurement. Best focus of light from lamp source on the sample was achieved by focusing the microscope to get a maximum peak intensity of the reflected signal from the sample. Figure 1a shows the OCs from the two substrates, exhibiting significant difference in profile.

To understand the difference between OCs from the two substrates, the OC spectra were calculated by multilayer optical interference method [9–14]. We considered a multilayer model with a trilayer structure containing air (refractive index $n_0 \approx 1$), SiO_2 film (complex refractive index $\tilde{n}_1$ [15] and thickness d_1), and Si substrate (complex refractive index $\tilde{n}_2$ [15]), as shown in Fig. 1b. The incident light was focused onto the sample by an objective with a given NA and the reflected light was collected by the same microscope objective. To take NA into account in the calculation, the p and s components of lights should be treated separately in calculation [10, 11]. The s and p polarizations are defined as shown in Fig. 1b. Thus, The total reflectivity intensity from SiO_2/Si substrate (R_{smp}) can be expressed as

$$R_{\mathrm{smp}} = \int_0^{\theta_{\arcsin(\mathrm{NA})}} \left(R^{\mathrm{s}}(\theta) + R^{\mathrm{p}}(\theta)\right)\pi \sin\theta \cos\theta \,\mathrm{d}\theta, \tag{1}$$

where the reflectivity intensity $R(\theta) = r(\theta)r(\theta)^*$ and the reflectivity amplitude $r(\theta) = E_{01}^{-}/E_{01}^{+}$. E_{01}^{+} and E_{01}^{-} are incident and reflective electric field component to or from the SiO_2/Si layers, respectively. Transfer matrix method [9, 10, 13] was used to calculate the OC of the trilayer dielectric structures. The electric field components in each medium of the trilayer are associated with each other as follows,

$$\begin{pmatrix} E_{10}^{\mathrm{s(p)},+} \\ E_{10}^{\mathrm{s(p)},-} \end{pmatrix} = \frac{1}{t_{01}^{\mathrm{s(p)}} t_{12}^{\mathrm{s(p)}}} \begin{pmatrix} 1 & r_{01}^{\mathrm{s(p)}} \\ r_{01}^{\mathrm{s(p)}} & 1 \end{pmatrix} \cdot \begin{pmatrix} \mathrm{e}^{\mathrm{i}\delta_1} & 0 \\ 0 & \mathrm{e}^{-\mathrm{i}\delta_1} \end{pmatrix} \begin{pmatrix} 1 & r_{12}^{\mathrm{s(p)}} \\ r_{12}^{\mathrm{s(p)}} & 1 \end{pmatrix} \begin{pmatrix} E_{21}^{\mathrm{s(p)},+} \\ 0 \end{pmatrix}, \tag{2}$$

where, $\delta_1 = 2\pi n_1 d_1 \cos\theta_1/\lambda$, t_{ij} and r_{ij} are transmission and reflection coefficients from the medium i to the medium j, respectively, which are different between the s and p polarizations of electric field components:

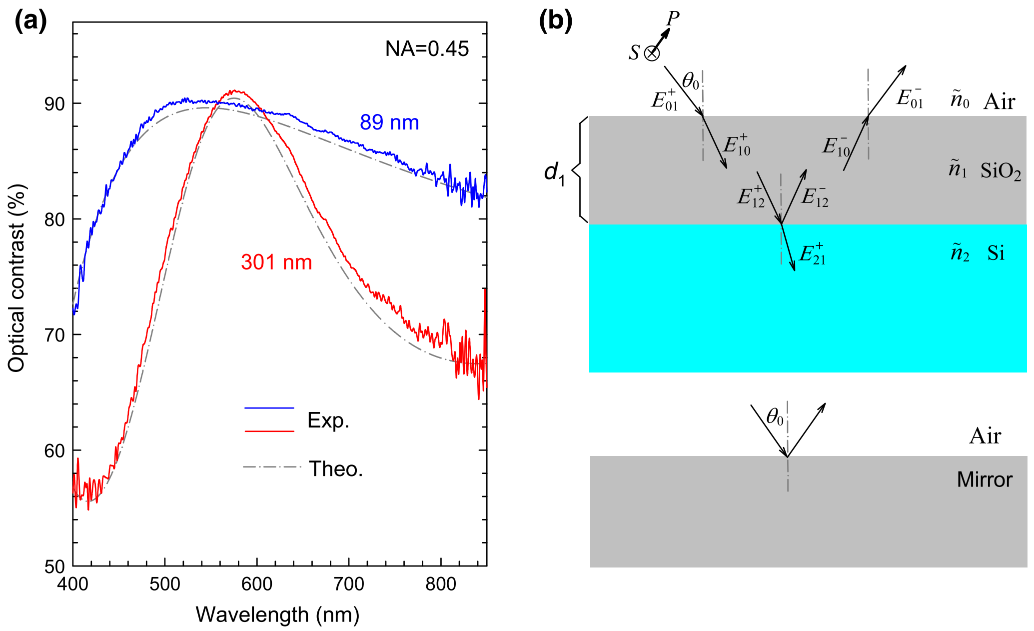

Fig. 1 (Color online) **a** Experimental (Exp., solid) and theoretical (Theo., dash-dotted) optical contrast curves of Si substrates covered with 301- and 89-nm SiO_2 layers, respectively. **b** Schematic diagrams of light incident into the trilayer structure containing air, SiO_2 layer and silicon substrate (top panel) and incident onto the surface of the mirror (bottom panel)

$$t_{ij}^{s} = \frac{2n_i\cos\theta_i}{n_i\cos\theta_i + n_j\cos\theta_j}, \tag{3}$$

$$r_{ij}^{s} = \frac{n_i\cos\theta_i - n_j\cos\theta_j}{n_i\cos\theta_i + n_j\cos\theta_j}, \tag{4}$$

$$t_{ij}^{p} = \frac{2n_i\cos\theta_i}{n_j\cos\theta_i + n_i\cos\theta_j}, \tag{5}$$

$$r_{ij}^{p} = \frac{n_j\cos\theta_i - n_i\cos\theta_j}{n_j\cos\theta_i + n_i\cos\theta_j}. \tag{6}$$

Based on the equations above, R_{smp} can be calculated once the thickness of the SiO_2 layer and NA of the objective are known. The OCs of SiO_2/Si with $h_{\mathrm{SiO_2}} = 89$ and 301 nm were calculated and shown in Fig. 1a for an objective of NA = 0.45, which are in good agreement with the experimental curves. This indicates that we can determine $h_{\mathrm{SiO_2}}$ of dielectric substrate by the OC measured using micro-Raman confocal system, whose spatial resolution can be down to the micrometer scale for a chosen objective.

The previous studies indicate that OC of FLG/SiO_2/Si multilayer is strongly dependent on NA of the used objective in the measurement [10]. For an objective 100× with NA = 0.9, a reduced NA is necessary to fit the experimental data because the objective lens with high NA may not be totally filled by the light or laser beam in the measurement [9, 10]. In Fig. 2, the OC of air/SiO_2/Si trilayer are measured using three Olympus objectives, 100× (NA = 0.90), 50× (NA = 0.55) and 50× (NA = 0.45). They exhibit a significant difference in profile and maximum amplitude, especially between NA = 0.45 and 0.90. The theoretical curves based on transfer matrix method are depicted in Fig. 2 as the dashed curves. The large difference between the experimental and theoretical curves for OC measured by objectives of NA = 0.55 and 0.90 suggests that it is better to choose the objective with NA smaller than 0.50 for $h_{\mathrm{SiO_2}}$ determination by OC measurement.

$h_{\mathrm{SiO_2}}$ of a SiO_2/Si substrate provided by a company usually has an error of about 5 %–10 %. Therefore, a simple method to determine $h_{\mathrm{SiO_2}}$ is very important. In the following text, we will further discuss the uncertainty of $h_{\mathrm{SiO_2}}$ determined by OC measurement as discussed above. For the two SiO_2/Si substrates with $h_{\mathrm{SiO_2}} = 89$ and 301 nm, we calculate the OC curves with several $h_{\mathrm{SiO_2}}$, as shown in Fig. 3. For the substrate with $h_{\mathrm{SiO_2}} = 89$ nm, we found that the theoretical thickness is 90 nm. If $h_{\mathrm{SiO_2}}$ is changed for ±5 nm, the line shape of the OC curve is similar and the maximum intensity of the theoretical curve shifts about 20 nm. For the substrate with $h_{\mathrm{SiO_2}} = 301$ nm, we found that the theoretical thickness is 302 nm. The maximum intensity shifts about 25 nm if $h_{\mathrm{SiO_2}}$ is changed for ±10 nm. Their profile always moves for a corresponding value in the long-wavelength direction. Such shift can be easily distinguished by the eye. For a careful comparison between the theoretical and experimental OC curves, one can determine $h_{\mathrm{SiO_2}}$ of SiO_2/Si substrates with an error

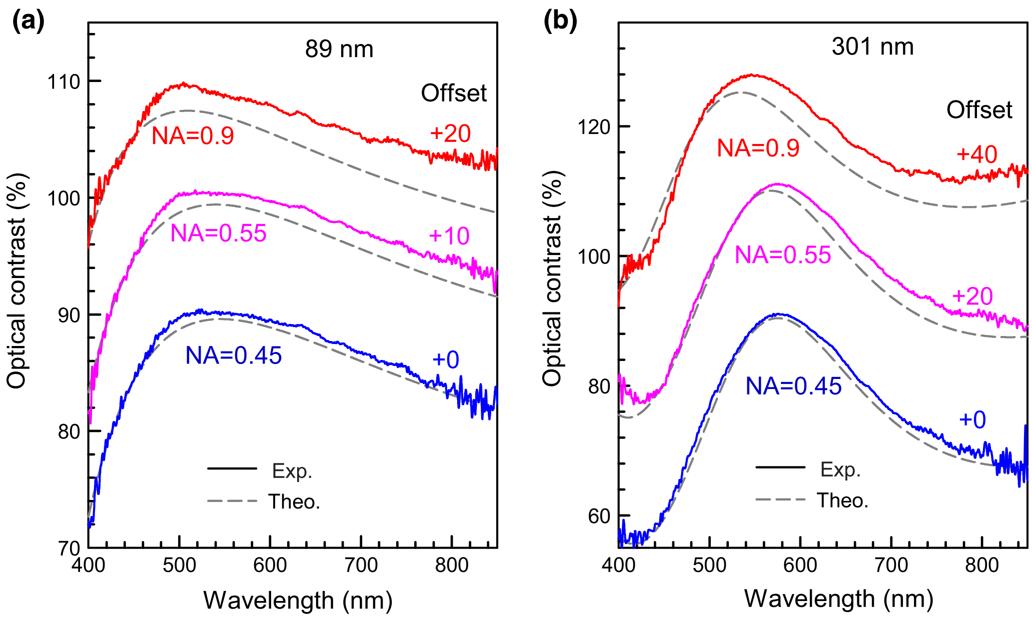

Fig. 2 (Color online) The experimental and theoretical optical contrast curves for $h_{SiO_2} = 89$ nm (**a**) and 301 nm (**b**). For each h_{SiO_2}, three objectives with NA of 0.45, 0.55 and 0.90 are used. The curves are offset for clarity

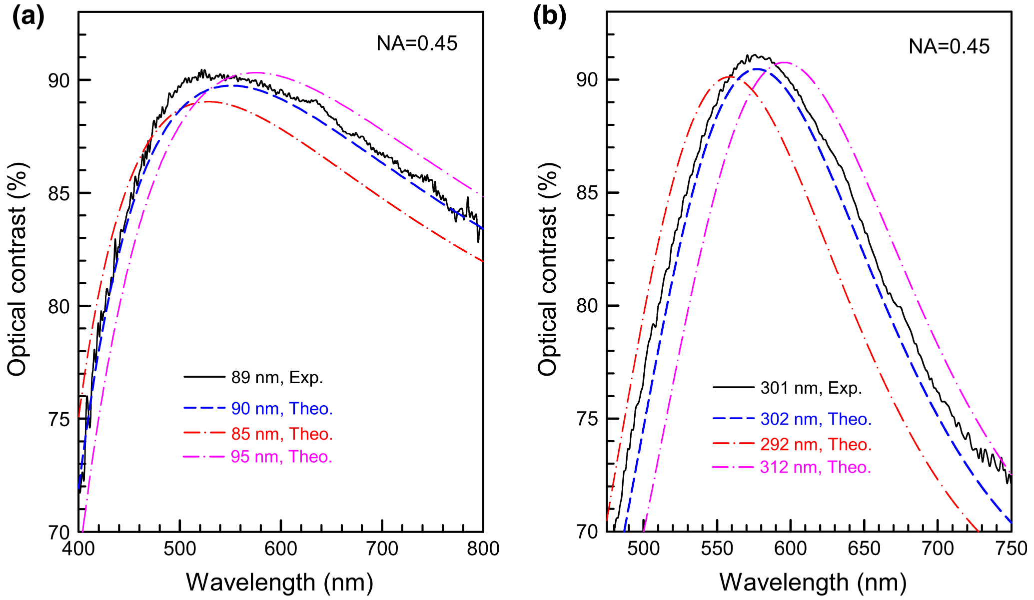

Fig. 3 (Color online) To compare the experimental (NA = 0.45) optical contrast curves of SiO_2/Si substrate with h_{SiO_2} of 89 nm (**a**) and 301 nm (**b**), three h_{SiO_2} are adopted theoretically to calculate the optical contrast curves

<3 % for $h_{SiO_2} \sim 100$ nm and 2 % for $h_{SiO_2} \sim 300$ nm. The excellent consistency between OC technique and spectroscopic ellipsometer provides an evidence that OC technique is an efficient and unambiguous way to identify the thickness of SiO_2 layer on Si wafer with a high accuracy.

Once the 2-D flakes had been grown or transferred onto SiO_2/Si substrate, some techniques, such as spectroscopic ellipsometer, are difficult to be applied for h_{SiO_2} and layer number of 2-D flakes in a 2-D flake/SiO_2/Si model [16]. However, OC measurement by micro-Raman confocal system via the objective can provide a high spatial resolution down to the micrometer scale. This suggests that once the bare SiO_2/Si area uncovered by 2-D flakes is up to the micrometer scale, one can use OC measurement to determine h_{SiO_2} of the SiO_2/Si substrate and further identify the layer number of 2-D flakes on the SiO_2/Si substrate.

To check the above-addressed applicability of the OC technique, as an example, we prepared graphene flakes by micromechanical cleavage of natural graphite on SiO_2/Si substrates whose h_{SiO_2} was undetermined initially. The inset of Fig. 4a shows one of typical optical images of the graphene flakes. Three graphene flakes were chosen for the OC measurement, whose results were depicted in Fig. 4a as solid lines. However, because h_{SiO_2} of the substrate is unknown, we cannot know the layer number of these flakes from the measurement. Then, the OC spectrum of the substrate uncovered by graphene flakes were measured by the objective with NA = 0.45, as shown in Fig. 4b. By comparing with the theoretical OC curve as addressed above, we can determine h_{SiO_2} of the substrate to be 286 nm, even though it is partially covered by graphene flakes. Based on h_{SiO_2} of 286 nm, we can calculate the OCs of the three graphene flakes on the substrate after considering an air/graphene/SiO_2/Si four-layer structure [10], as depicted in Fig. 4a by dashed lines. In the OC calculation of graphene flakes, we used the most widely accepted complex refractive index for 2LG–4LG [17], and therefore, the absorption of 2.3 % of white light for each graphene layer has been considered in the calculation by transfer matrix formalism. The three graphene flakes are bilayer (2LG), trilayer (3LG) and four-layer (4LG) graphenes, respectively. Their Raman spectra of the three flakes were measured, as shown in Fig. 4c. Their 2D modes are identical to those of previous results [18].

It should be noted that the maximum intensity of the theoretical OC curves for 2LG–4LG is almost identical to that of the experimental ones; however, all three theoretical OC profiles slightly shift toward the short-wavelength direction for about 10 nm. This small deviation between the experimental and theoretical OC curves of graphene flakes may be ascribed to that the reported complex refractive index of graphene layers is not still fully determined yet [17, 19, 20]. In the OC calculation of graphene flakes, we used the most widely accepted one for 2LG–4LG [17]. However, complex refractive index of graphene flakes should be slightly layer number dependent. Given that only 2–4 layers of graphene were investigated during the measurement, the impurities adsorbed at exfoliated graphene surface under ambient condition, whose thickness is comparable to that of monolayer graphene, may be also possible to introduce such a deviation according to recent studies [21, 22]. Because the measured OCs for 2LG–4LG are quite different, this small deviation is acceptable and does not induce any uncertainty in the layer number identification of FLG on SiO_2/Si substrate.

4 Conclusions

Optical contrast technique has been demonstrated to determine the thickness of SiO_2 film on Si substrate, which has been widely used as the supporting substrate for 2-D materials. This method is a simple, fast and nondestructive technique with a high accuracy and a high laterally spatial resolution down to the micrometer scale. Therefore, it can be used to determine h_{SiO_2} of small-sized SiO_2/Si substrate

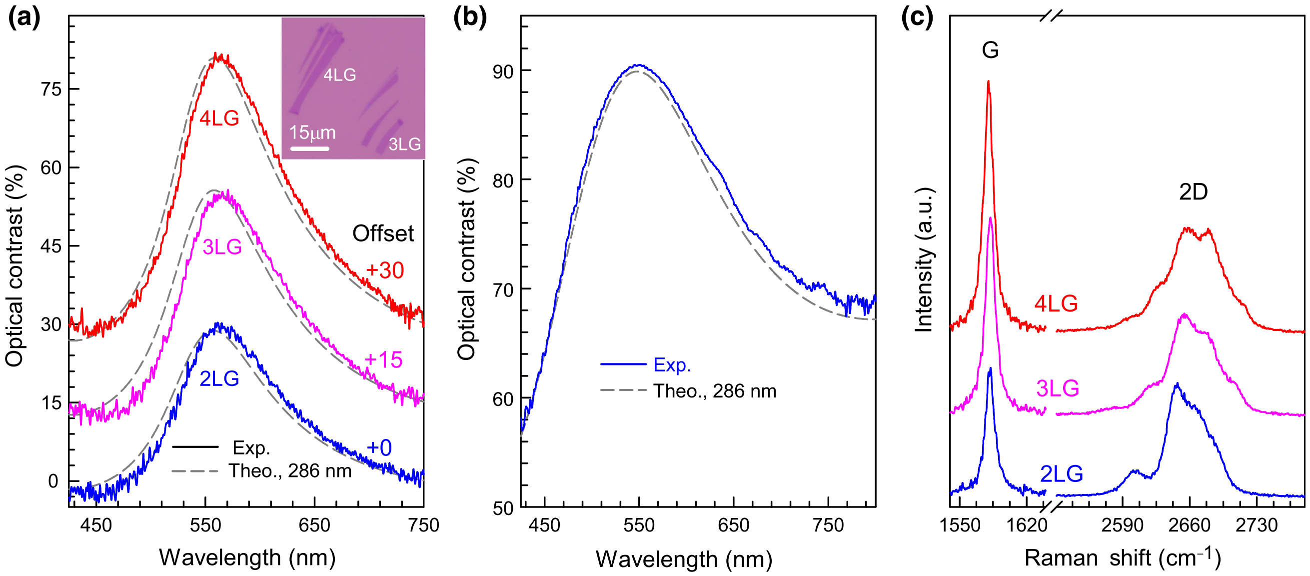

Fig. 4 (Color online) **a** The experimental and theoretical optical contrast curves of 2LG, 3LG and 4LG flakes on SiO_2/Si substrate, whose h_{SiO_2} is determined by the optical contrast curve of SiO_2/Si substrate itself (**b**). The optical image of 3LG and 4LG flakes is depicted in the inset of (**a**). The dashed line in (**b**) is the theoretical curve based on $h_{SiO_2} = 286$ nm. (**c**) Raman spectra of the 2LG–4LG in the G- and 2D-band range. The curves in (**a**) and (**c**) are offset for clarity

or of SiO_2/Si substrate that has been covered by 2-D crystal flakes. As a protyle of this application, we determined the layer number of graphene flakes on SiO_2/Si substrate, whose h_{SiO_2} is not determined initially, only by the OC technique with micro-Raman confocal system. This technique can be extended to other dielectric multilayer substrate and layer-number identification of other 2-D crystal flakes on the dielectric multilayer substrate.

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Conflict of interest The authors declare that they have no conflict of interest.

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