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Large-Area Few-Layer Graphene Film Determination by Multispectral Imaging Microscopy

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A multispectral imaging method for the rapid and accurate identification of few-layer graphene using optical images is proposed. Commonly rapid identification relies on optical interference effects which limits the choice of substrates and light sources. Our method is based on the comparison of spectral characteristics with principle components from a database which is populated by correlation of micro-Raman registration, spectral characteristics, and optical microscopy. Using this approach the thickness and extend of different graphene layers can be distinguished without the contribution of the optical interference effects and allows characterization of graphene on glass substrates. The high achievable resolution, easy implementation and large scale make this approach suitable for the in-line metrology of industrial graphene production.

(S1)

This study was designed to construct a set of analysis systems for the graphene film with different layers. The experimental processes are shown in Fig. S1 At the beginning of the experiment, a database of the spectral characteristics of the graphene with different layers should be established. Later, new samples for analysis will be compared. The procedure for setting up the database is as follows. The position of each layer of the graphene film sample prepared was measured with the micro-Raman spectrometer, and the image at the same position was captured with an optical microscope and a CCD (Image Capture System, ICS). From the CCD images obtained, the spectral characteristics (380 nm–780 nm) of the graphene film with various layers can be obtained with the MSIM technique. Then, using PCA and PCS, the condition of various layers can be defined, thereby completing the database.[25-28] When new graphene samples are to be analyzed, they will be placed under an optical microscope to capture their surface images with the CCD. However, products will generate high-frequency noise because of the electronic signal transmission.[18] Thus, the image is median-filtered to remove the noise, and the spectral value of each pixel can be obtained with the MSIM technique. Its discriminant with each number of layers of graphene film in the database is calculated through the main component score analysis to determine the number of layers of the graphene film at the pixel position. The graphene films with varying number of layers in the image are clearly marked with different colors.

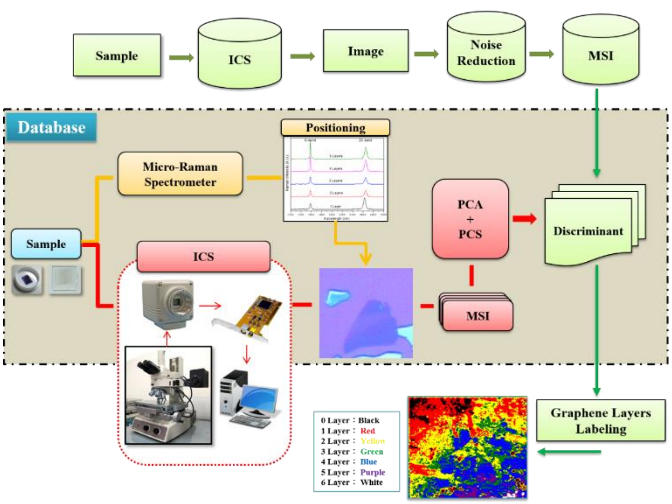

Fig. S1 Schematic of the proposed method used to detect few-layer graphene.

(S2)

Fig. S2(a) and S2(c) are the images at positions 1 and 2 of specimen A under 40× magnification, respectively. Figs. S2(b) and S2(d) are the images of the different number of layers that are median-filtered results in Fig.s S2(a) and S2(c), respectively. Figs. S3(a) and S3(d) are the images at positions 1 and 2 of specimen B under 40× magnification, respectively. Figs. S3(b) and S3(e) are the images of the different number of layers that are median-filtered and marked results with different colors in Figs. S3(a) and S3(d), respectively. Figs.S3(c) and S3(f) represent the 41 × 41 um^2 Raman mapping of Figs.S3(a) and S3(d), respectively. The analytical results indicate that the contrast of the SiO_2 (300 nm)/Si substrate is high, so the analytical results are similar to those obtained under 20× magnification. When the analysis is conducted on a glass substrate, the impurities on the sample are more obvious after magnification, which may interfere with the analytical results. To determine the accuracy of the results, Raman scanning is conducted on the sample. The trends of each layer still exist, but the impurities on the surface of the sample are quite difficult to overcome.

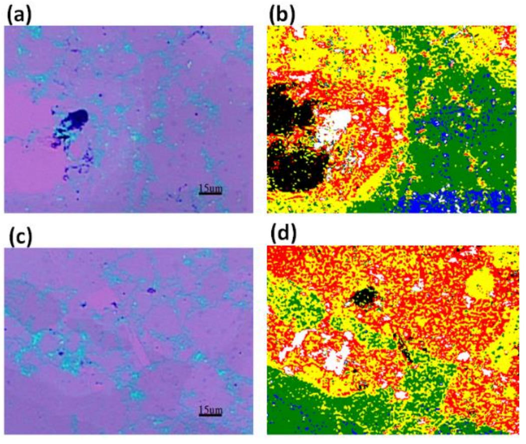

Fig. S2 (a) The image of position 1 of sample A under 40× magnification; (b) image of (a) with different layers marked with various colors after median filtering; (c) image of position 2 of sample A under 40× magnification; (d) image of (c) with different layers marked with various colors after median filtering.

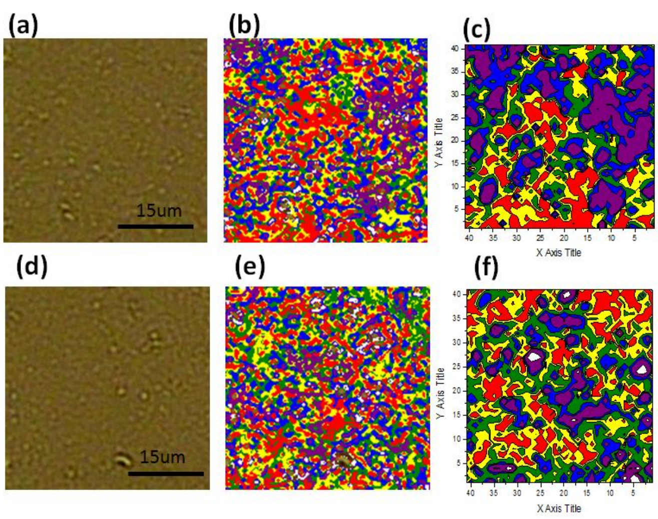

Fig. S3 (a) The image of position 1 of sample B under 40× magnification; (b) image of (a) with different layers marked with various colors after median filtering; (c) analytical results of the location of (a) with Raman imaging; (d) image of position 2 of sample B under 40× magnification; (e) image of (d) with different layers marked with various colors after median filtering; (f) analytical results of the location of (d) with Raman imaging.

(S3)

Validating with Fresnel equation

With the optical effect produced by graphene on the SiO_2 (300 nm)/Si substrate, the contrast C(λ) of the graphene film and the substrate can be derived from the Fresnel equation under the conditions of normal incident light source.

$$C(\lambda) = \frac{R_0(\lambda) - R(\lambda)}{R_0(\lambda)} \quad \text{(s-1)}$$

where

$$R_0(\lambda) = |r_0(\lambda)|^2 \quad \text{(s-2)}$$

$$R(\lambda) = |r(\lambda)|^2 \quad \text{(s-3)}$$

where R_0 and r_0 represent the reflected light intensity and reflectivity on the air/SiO_2/Si substrate, respectively. Additionally, R and r represent the corresponding values on the air/graphene/SiO_2/Si substrate. The light reflectivity of the two- and three-layer systems is described by the following formula:

$$r_0(\lambda) = \frac{r_{02} + r_{23}e^{-2i\Phi_2}}{1 + r_{02}r_{23}e^{-2i\Phi_2}} \quad \text{(s-4)}$$

$$r(\lambda) = \frac{r_{01} + r_{01}r_{12}r_{23}e^{-2i\Phi_2} + r_{12}e^{-2i\Phi_1} + r_{23}e^{-2i(\Phi_1+\Phi_2)}}{1 + r_{12}r_{23}e^{-2i\Phi_2} + r_{01}r_{12}e^{-2i\Phi_1} + r_{01}r_{23}e^{-2i(\Phi_1+\Phi_2)}} \quad \text{(s-5)}$$

where

$$r_{ij} = \frac{n_i - n_j}{n_i + n_j} \quad (0 \le i, j \le 3) \quad \text{(s-6)}$$

n_0, n_1, n_2, and n_3 represent the refractive indices of air, graphene, SiO_2, and Si, respectively.

$$\Phi_{1,2} = \frac{2\pi n_{1,2} d_{1,2}}{\lambda} \quad \text{(s-7)}$$

Equation (s-7) is the phase difference of light when passing through the medium, which is the path difference formed caused by two adjacent interfering beams. $\Phi_{1,2}$represents the phase difference of light when passing through graphene and SiO_2, respectively. $d_1 = N \times d$ represents the thickness of the layer of graphene. The thickness of the graphene with single layer is d=0.335 nm, as mentioned in Ref. 8, and d_2 indicates the SiO_2 thickness. Through calculation with the above formula, the contrast of the graphene with different layers with the substrate can be calculated by substituting the intensity of the reflected light into Equation (s-1), as shown in Fig. S4(a) in Ref. 19.

Our MSIM technology can also simulate the intensity of the reflection spectrum of the various layers of the graphene film and the substrate. With Equation (s-1), the contrast of the graphene film with 1–4 layer on the substrate can be obtained [Fig. S4(b)]. The results indicated that our simulated contrast results are similar to the theoretical value formula. Images under 650, 550, and 450 nm are captured, and the images under a single-wavelength signal in each pixel are shown in Fig. S5. From the image under 550 nm wavelength, different layers of graphene with obvious contrast are observed. Thus, our proposed method for analyzing the different graphene film layers on the SiO_2 (300 nm)/Si substrate is feasible.

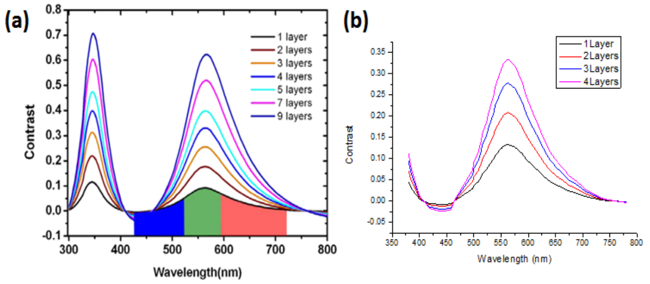

Fig. S4 (a) Theoretical calculation of ratio between the graphene film with 1–4 layers on SiO_2/Si substrate and the substrate[11]; (b) simulated result of the MSIM used in this study.

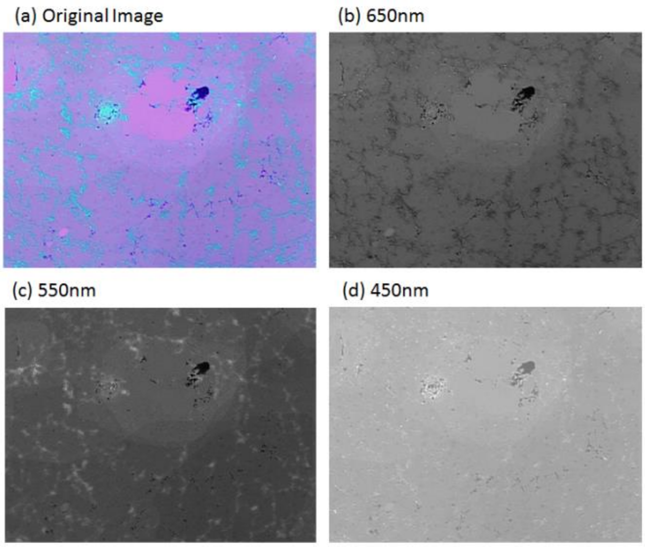

Fig. S5 (a) The image of position 1 of sample B under 40× magnification; (b) image of (a) with different layers marked with various colors after median filtering; (c) analytical results of the location of (a) with Raman imaging; (d) image of position 2 of sample B under 40× magnification; (e) image of (d) with different layers marked with various colors after median filtering; (f) analytical results of the location of (d) with Raman imaging.