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# Versatile optical determination of two-dimensional atomic crystal layers

Bangjun Ma<sup>a</sup>, Peiqi Wang<sup>a</sup>, Shizhao Ren<sup>a</sup>, Chuancheng Jia<sup>a</sup>, Xuefeng Guo<sup>a, b, \*</sup>

<sup>a</sup> Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

<sup>b</sup> Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, PR China

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#### ABSTRACT

An efficient method has been developed to facilitate the identification of the layer number of twodimensional atomic crystals from their optical images. By analyzing the image contrasts of twodimensional atomic crystals with different layers, such as graphene, hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS<sub>2</sub>), on silicon substrates, it was found that the image contrasts of these two-dimensional materials showed the distinct relation with the layer number, which was well explained by the theoretical analysis. This method proved the importance of proper choices of the substrate to achieve a clear linear relation between the image contrast and the layer number. Since the method only relies on a standard optical microscope with a charge-coupled device (CCD) camera and simple calculation of the contrast from the optical images, the entire process of layer identification can be finished in a short time and with low cost, thus speeding up the exploration of the big family of twodimensional atomic crystals.

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# 1. Introduction

Graphene has stimulated considerable interest from a variety of research fields since its first discovery in 2004 [1] because it possesses various remarkable physical and chemical properties [2-6]and opened up a new world of the two-dimensional atomic crystal family [7–11]. In particular, the unique electronic structures of these two-dimensional materials are currently one of the major research focuses in fundamental physics and electronic/optoelectronic device applications, for example quantum Hall effect [12,13] and high-performance wide-band photodetectors [14–16], which require high-quality two-dimensional atomic crystals. Until now, the best quality of two-dimensional atomic crystals is still provided by the pristine method, micromechanical cleavage, in spite of massive studies and ongoing attempts at the growth of large-area, high-quality materials [17-20]. However, the layer numbers and locations of these cleaved sheets are randomly controlled. Moreover, the layer number of two-dimensional atomic crystals assembled through weak Van der Waals interaction may significantly affect their electronic structures, which leads to the different electrical behaviors and corresponding applications. For example, the conduction band of single-layer graphene touches its valence band at the so-called Dirac point where electrons obey the linear dispersion relation and behave as massless Dirac fermions. However, for bilayer graphene, the dispersion relation is guasi-parabolic near the K point and an energy gap emerges when an electric field is applied perpendicular to the stacked layers, promising potential application in future electronic devices [21]. Therefore, in this regard, the identification of the number of the stacked layers is an important issue. In general, Raman spectroscopy [22,23], atomic force microscopy (AFM) and transmission electron microscopy (TEM) [24] are accurate tools to characterize the layered structures. However, these tools are not always convenient for various reasons such as instrument expense, time cost and complex operation. Therefore, they seem not ideal choices to accomplish the layer identification task, especially for those in frequent need of identification. In comparison, optical microscopes are popular and basic scientific tools in a wide range of research fields with the advantages of the least expense and easiest operation. An effective method based on optical microscopes would render the layer identification convenient and comfortable, promising a





<sup>\*</sup> Corresponding author. Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China. *E-mail address:* guoxf@pku.edu.cn (X. Guo).

competitive alternative.

As the most investigated two-dimensional atomic crystal, the visibility of graphene on silicon substrates through the optical microscope is a strong proof of the existence of stable single-layer graphene in ambient condition. Previous studies [25-28] have revealed the origin of the optical contrast of graphene on silicon substrates based on both experimental contrast spectra and the theory of electromagnetic wave propagation at the interface, i.e., Fresnel's law. In brief, the optical contrast of graphene stems from the slightly changed light interference and corresponding changed intensity of reflected light in comparison with that for the bare substrate, which is determined by three main factors: the thickness of graphene sheets and SiO<sub>2</sub> layer (semi-infinite for silicon), the refractive indexes of graphene sheets, SiO<sub>2</sub> layer and underneath silicon, and the wavelength of incident light. Moreover, the refractive index of graphene is layer dependent, in spite that only the values of single-layer graphene and graphite are available [25,26]. Precisely but inconveniently, the contrast spectra and theoretical analysis based on Fresnel's law still seem rather complex and fail to be a practical method to identify graphene layers, letting alone other two-dimensional atomic crystals.

In this work, we proposed a simple and practical method to optically identify the layer number of two-dimensional atomic crystals. The method defined a term of image contrast from the optical images of these layered materials, which linearly changed with the layer number upon proper choices of the substrate without complex mathematical analysis and numerous parameters. To prove its universality, we first calculated the image contrasts of different layers of graphene, h-BN and MoS<sub>2</sub>, which are representative semi-metal, insulator and semiconductor, respectively, prepared by micromechanical cleavage and obtained the distinct relation between the image contrast and layer number. In combination with theoretical analysis based on Fresnel's law, the distinction was then well explained and a general empirical rule was hence summarized to guide the choice of the substrate to achieve the best linear relation. This method could help solve the issue of optical identification of two-dimensional atomic crystal layers and evolve to be a regularly used tool finally.

# 2. Experimental methods

The process of layer identification is presented as follows. Graphene samples were prepared by micromechanical cleavage of commercially available Kish graphite and transferred onto silicon substrates with a 300 nm-thick SiO<sub>2</sub> layer. A standard optical microscope (Olympus BX51TRF with a 50  $\times$  , 0.8 numerical aperture (NA) objective) with a CCD camera (Olympus DP71) was used to acquire optical images of graphene samples. Under mild white light illumination, the exposure time was set constant in replace of the auto mode. Raman spectroscopy measurements were carried out with the excitation laser beam of 514 nm (Horiba Lab Ram HR800). The Raman band of a silicon wafer at 520 cm<sup>-1</sup> was used as a reference to calibrate the spectrometer. AFM was also used to acquire height information in tapping mode (Bruker Dimension Icon).

# 3. Results and discussions

Fig. 1a illustrates a representative image of graphene samples of different layers in the same area, which can be distinguished clearly. A free image processing software (ImageJ, software version of 1.47) was then used to calculate the image contrast (*C*) from the optical images by the following equation:

$$C = \frac{G_{sub} - G_{mater}}{G_{sub}} \tag{1}$$

where  $G_{mater}$  and  $G_{sub}$  are the grey values of the two-dimensional atomic crystals and the substrate in selected areas, respectively, which can be analyzed by the function of histogram in the software. To minimize the inhomogeneous reflected brightness caused by the optical microscope and camera system,  $G_{sub}$  was obtained from the substrate area adjacent to the graphene sheet and the standard deviation of analyzed grey values in the selected area was controlled below 0.5. For example, the grey value of graphene with the lightest contrast illustrated in Fig. 1a is 166.35, and that goes for 170.25 in a neighboring substrate area, so the calculated image contrast is ~2.3%. Similarly, the other layers of graphene sheets correspond to contrast values of ~4.2%, ~6.3%, ~7.9%, and ~9.7% with standard deviations below 0.05% according to the formula of deviation transfer. To correlate these values with the layer numbers, Raman spectroscopy and AFM were utilized to precisely identify the number of graphene layers. Raman spectra were taken from the graphene sheets with different image contrasts according to our calculation, and the results are shown in Fig. 1b. Single-layer graphene is easily recognized by its sharp and symmetric 2D band  $(\sim 2670 \text{ cm}^{-1})$  and the highest 2D/G ratio, and its image contrast is ~2.3%. Fig. 1c presents the G band (~1580  $\text{cm}^{-1}$ ) mapping spectra of the sample in Fig. 1a. Once single-layer graphene is identified, it is easy to assign the other graphene layers from the gradual increase of G band to the increasing image contrast. The same graphene sample was then characterized by AFM after Raman spectroscopic measurements, and the result is shown in Fig. 1d. The height of single-layer graphene on the silicon substrate identified (already identified by Raman spectroscopy) is ~1.20 nm due to the offset of instrument, and a step of ~0.32 nm in height is obviously found as the graphene layer becomes thicker (Fig. 1e and f). On the basis of these results, it is inferred that through both Raman spectra and height information, the image contrast of graphene sheets increases with the layer number, at least in the range of few-layer graphene.

We then carried out calculations of about 1000 graphene samples (Fig. 2a) and made a statistical histogram of image contrasts. As illustrated in Fig. 2b, there exist six narrowly distributive peaks resulting from six different layers of graphene sheets, according to previous Raman spectroscopy and AFM characterizations. Mean values were extracted from these six peaks and fitted by a linear equation (red curve in Fig. 2c):

$$C = 0.0188 N + 0.0057 (N \le 6) \tag{2}$$

which demonstrates that the image contrast of graphene shows the linear increase with its layer number. To avoid the occasionality from the particular microscope system and prove the reproducibility, we used another microscope system (Nikon LV 100D with a Smart 200 Digital Camera, Powgen Engineering Co. Ltd.) to acquire optical images of the same graphene sheet shown in Fig. 1a, and found that the method still worked well only with a correction of the parameters in the linear equation (blue curve in Fig. 2c), which will be explained later.

To demonstrate the universality, considering the electronic structure, we chose h-BN and MoS<sub>2</sub>, representative twodimensional insulator and semiconductor nanomaterials, to check whether the linear relation still exists. Both materials were prepared in the same way as used for graphene (Fig. 3a and c). According to the statistical histogram of about 200 h-BN sheets (Fig. 3b), the image contrast decreases with increasing the layer number with an average step of about 0.5% (Fig. 3a). The situation is



Fig. 1. Optical image (a) and Raman spectra (b) of graphene of one to five layers. Scale bar is 10 µm. (c) Raman images plotted by the intensity of G band obtained from the dashed rectangles shown in Fig. 1a. Scale bars are 5 µm. AFM images (d) and corresponding height profiles (e) and (f) of graphene obtained from the dashed rectangles shown in Fig. 1a. Scale bars are 4 µm. (A colour version of this figure can be viewed online.)



Fig. 2. (a) Illustration of graphene sheets with various image contrasts. Scale bars are 10 µm. (b) Statistical histogram of image contrasts of graphene. (c) Linear fittings between the image contrast of graphene and its layer number from the current microscope system (red) and another microscope system (blue). (A colour version of this figure can be viewed online.)

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relatively complex for MoS<sub>2</sub>. The image contrast increases first followed by an average decrease step of about 0.6% as the MoS<sub>2</sub> sheets become thicker (Fig. 3c and d), in agreement with previous study [29].

To clarify the distinction among three materials, a simple model of a tri-layer structure consisting of two-dimensional atomic crystal, a SiO<sub>2</sub> layer and a semi-infinite silicon substrate (Fig. 4a) is used to simulate the real condition. According to Fresnel's law, the reflectivity (*R*) under mild light illumination can be written as:

$$R = \left[ \frac{r_1 e^{i(\Phi_1 + \Phi_2)} + r_2 e^{-i(\Phi_1 - \Phi_2)} + r_3 e^{-i(\Phi_1 + \Phi_2)} + r_1 r_2 r_3 e^{i(\Phi_1 - \Phi_2)}}{e^{i(\Phi_1 + \Phi_2)} + r_1 r_2 e^{-i(\Phi_1 - \Phi_2)} + r_1 r_3 e^{-i(\Phi_1 + \Phi_2)} + r_2 r_3 e^{i(\Phi_1 - \Phi_2)}} \right]^2$$

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

$$\Phi_1 = \frac{2\pi n_1 d_1}{\lambda}, \quad \Phi_2 = \frac{2\pi n_2 d_2}{\lambda}$$
(3)

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Fig. 3. (a, c) Illustration of h-BN (a) and MoS<sub>2</sub> (c) sheets with various image contrasts. Scale bars are 5  $\mu$ m. (b, d) Statistical histogram of image contrasts of h-BN (b) and MoS<sub>2</sub> (d). (A colour version of this figure can be viewed online.)



**Fig. 4.** (a) Illustration of the theoretical model of a tri-layer structure. (b–d) Theoretical optical contrasts of one to ten layers of graphene, h-BN and MoS<sub>2</sub> on silicon substrates with 300 nm-thick SiO<sub>2</sub> layers, respectively. (A colour version of this figure can be viewed online.)

where  $n_0$ ,  $n_1$ ,  $n_2$ ,  $n_3$  are the complex refractive indexes of air, the two-dimensional atomic crystal, the SiO<sub>2</sub> layer, and the silicon substrate, respectively.  $d_1$  and  $d_2$  represent the corresponding thickness (0.335 nm, 0.333 nm, and 0.65 nm per layer for graphene, h-BN, MoS<sub>2</sub> and semi-infinite for silicon, respectively).  $\lambda$  is the wavelength of incident light. Here, a term of optical contrast ( $C_{th}$ ) is defined as follows:

$$C_{th} = \frac{R_{sub} - R_{mater}}{R_{sub}} \tag{4}$$

where  $R_{mater}$  and  $R_{sub}$  are the reflectivity of the two-dimensional atomic crystal and the substrate. Then, the optical contrasts of

graphene, h-BN and MoS<sub>2</sub> of one to ten layers on silicon substrates with a 300 nm-thick SiO<sub>2</sub> layer are plotted as a function of the wavelength (Fig. 4b–d) [25,30–32]. It is interesting to find that the optical contrast of graphene increases approximately linearly with the layer number in almost the whole wavelength range in spite of different contrast values at each wavelength, in agreement with the experimental part. The plotting curves of either h-BN or MoS<sub>2</sub> mainly consist of a positive part and a negative part, the offset of which explains the little difference of the image contrast between two consecutive layers of h-BN or MoS<sub>2</sub>. For h-BN, the negative part predominates slightly in the whole range of wavelength, leading to a slight decrease of image contrast. For MoS<sub>2</sub>, the positive part contributes more to the image contrast at fewer layers while the negative part gradually takes over as the layer number increases, resulting in a maximum point in the image contrast. It should be noted that the experimental image contrast values were calculated from the grey values of the optical images and they are not directly the optical contrast from the theoretical reflectivity. Although the connection between the image contrast and optical contrast is missing because of the unknown spectrum of the light source and light response of the CCD camera, the image contrast is thought to be the average effect of the optical contrasts at all wavelengths (also see the Supporting Information). The connection only determines the weight factors of the optical contrasts during the transformation, but does not harm the tendency of optical contrast with the layer number at each wavelength. As mentioned in the experimental part, the linear relation between graphene's image contrast and the layer number still works in a different microscope system with a correction of parameters in the linear equation. This should be ascribed to different weight factors when the spectrum of the light source and light response of the CCD camera are changed. Note that the largest layer numbers of graphene and h-BN that can be identified through this method is 6 and 10, respectively, since the changes of the image contrasts are less and less obvious with further increasing the layer number.

On the basis of above-mentioned analysis, an empirical rule is proposed to instruct one to choose proper substrates in order to tune the linear relation between the image contrast and the layer number and identify these layered materials clearly. The first point is that the optical contrasts of these layered materials on proper substrates should change as the laver number increases along a single direction in the entire or most range of the wavelength, avoiding the non-unidirectional change of optical contrast and the little contrast difference caused by the offset between positive and negative parts. The second is that the spacing of optical contrast values of different layer numbers should be large enough to be distinguished clearly from each other. Guided by the rule, more curves of these materials as well as tungsten diselenide  $(WSe_2)$  [33] and black phosphorus (BP) [34] on silicon substrates with various thickness of the SiO<sub>2</sub> layer are plotted (Figs. S1–S5). It is predictable that silicon substrates with a 90 nm- or 300 nm-thick SiO<sub>2</sub> layer are suitable to identify graphene layers. Similarly, 145 nm for h-BN, 150 nm for MoS<sub>2</sub> and WSe<sub>2</sub>, and 50 nm or 270 nm for BP are the proper choices. In these cases, the image contrasts are believed to be linearly changing with the layer number.

#### 4. Conclusions

In summary, we proposed a simple and practical optical method to identify the layer number of two-dimensional atomic crystals on silicon substrates and predict the proper choices of substrates to distinguish the contrast differences. This method only relies on an optical microscope and simple calculation of the image contrast. We are firmly of the opinion that this efficient optical method is ready to be widely used to facilitate the investigation of the big family of two-dimensional atomic crystals.

# **Conflict of interest**

The authors declare no conflict of interest.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.08.008.

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