



Versatile optical determination of two-dimensional atomic crystal layers



Bangjun Ma^a, Peiqi Wang^a, Shizhao Ren^a, Chuancheng Jia^a, Xuefeng Guo^{a, b, *}

^a 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

^b Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, PR China

ARTICLE INFO

Article history:

Received 21 June 2016

Received in revised form

3 August 2016

Accepted 4 August 2016

Available online 15 August 2016

ABSTRACT

An efficient method has been developed to facilitate the identification of the layer number of two-dimensional atomic crystals from their optical images. By analyzing the image contrasts of two-dimensional atomic crystals with different layers, such as graphene, hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS₂), 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 two-dimensional atomic crystals.

© 2016 Elsevier Ltd. All rights reserved.

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 quasi-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

* 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 SiO₂ layer (semi-infinite for silicon), the refractive indexes of graphene sheets, SiO₂ 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 MoS₂, 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 SiO₂ layer. A standard optical microscope (Olympus BX51TRF with a 50 ×, 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⁻¹ 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:

$$C = \frac{G_{sub} - G_{mater}}{G_{sub}} \quad (1)$$

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 (~2670 cm⁻¹) and the highest 2D/G ratio, and its image contrast is ~2.3%. Fig. 1c presents the G band (~1580 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):

$$C = 0.0188 N + 0.0057 \quad (N \leq 6) \quad (2)$$

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 MoS₂, representative two-dimensional 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

Download English Version:

<https://daneshyari.com/en/article/7849341>

Download Persian Version:

<https://daneshyari.com/article/7849341>

[Daneshyari.com](https://daneshyari.com)