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Rapidly counting atomic planes of ultra-thin $MoSe_2$ nanosheets ($1 \leq n \leq 4$) on SiO_2/Si substrate

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Abstract The optical, thermal and electrical properties of ultra-thin two-dimensional (2D) crystal materials are highly related to their thickness. Therefore, identifying the atomic planes of few-layer crystal materials rapidly is crucial to fundamental study. Here, a simple technique was demonstrated based on optical contrast for counting atomic planes (n) of few-layer $MoSe_2$ on SiO_2/Si substrates. It is found that the optical contrast of single-layer $MoSe_2$ depends on light wavelength and thickness of SiO_2 on Si substrate. The data calculated based on a Fresnel law-based model as well as atomic force microscopy (AFM) measurements fit well with the values measured by spectroscopic ellipsometer. Furthermore, the calculated and measured contrasts were integral and plotted, which can be used to determine the $MoSe_2$ atomic planes ($1 \leq n \leq 4$) accurately and rapidly.

Keywords Thickness identification; Optical contrast; $MoSe_2$; Optical microscopy

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1 Introduction

Since the discovery of mechanical exfoliated graphene in Manchester in 2004 [1, 2], two-dimensional (2D) materials have attracted much interest [3]. However, graphene does not have a native bandgap, leading to the prosperity of other 2D semiconducting materials, such as the transition-metal dichalogenides [4–7]. Transition-metal dichalogenides have demonstrated many extraordinary optical, thermal, magnetic and electrical properties and are ready for various applications [8–10]. Recently, single-layer $MoSe_2$ has been exfoliated onto SiO_2/Si substrate. Determined by photoluminescence measurements, $MoSe_2$ displayed good thermal stability with a direct bandgap of 1.55 eV [11]. In addition, single-layer $MoSe_2$ was proved to have electrocatalytic activity [8]. Like graphene, these properties are highly related to thickness [8, 12, 13]. However, 2D $MoSe_2$ produced by mechanical exfoliation not only is single layer but also has a lot of thick flakes. Therefore, it is crucial to find a method to identify the thickness of 2D $MoSe_2$ accurately and rapidly.

Up to now, many methods have been studied, such as atom force microscope (AFM), Raman spectroscopy and optical microscopy (OM) [12–14]. Accurate enough, AFM and Raman spectroscopy [12] are commonly used to measure the thickness of 2D nanosheet, but they consume too much time, which might lead to the pollution of the samples before measurements [4, 13]. Compared with AFM and Raman spectroscopy, the optical technique performs more rapidly and conveniently [10, 15–17].

In this paper, OM method was used to identify the thickness of 2D $MoSe_2$ nanosheet with a few layers. Furthermore, the calculated and measured contrast was integral, which can be used to determine the $MoSe_2$ layer number accurately and rapidly.

2 Theoretical calculation

The key to identifying the thickness of 2D $MoSe_2$ nanosheet rapidly and accurately by OM is to correlate its thickness with its optical contrast. In order to calculate the contrast, it was considered the case of normal light incidence from air onto a three-layer structure consisting of two films ($MoSe_2$/SiO_2) on top of a third semi-infinite film (Si), as shown in Fig. 1. The optical contrast ($C(\lambda)$) of $MoSe_2$ on SiO_2/Si substrate was calculated by Fresnel equation under normal incident conditions [18]

$$C(\lambda) = \frac{I_0(\lambda) - I(\lambda)}{I_0(\lambda)} \tag{1}$$

where $I_0(\lambda) = |r_0(\lambda)|^2$ and $I(\lambda) = |r(\lambda)|^2$ are the reflected light intensities of the SiO_2/Si and $MoSe_2$/SiO_2/Si system, in which r is complex amplitude reflectance. Both intensities are light wavelength (λ) dependent.

$$r_0(\lambda) = \frac{r_2' + r_3 e^{-2i\delta_2}}{1 + r_2' r_3 e^{-2i\delta_2}} \tag{2}$$

$$r(\lambda) = \frac{r_1 + r_2 e^{-2i\delta_1} + r_3 e^{-2i(\delta_1+\delta_2)} + r_1 r_2 r_3 e^{-2i\delta_2}}{1 + r_1 r_2 e^{-2i\delta_1} + r_2 r_3 e^{-2i\delta_2} + r_1 r_3 e^{-2i(\delta_1+\delta_2)}} \tag{3}$$

where $r_2' = \frac{n_0 - n_2}{n_0 + n_2}$, $r_1 = \frac{n_0 - n_1}{n_0 + n_1}$, $r_2 = \frac{n_1 - n_2}{n_1 + n_2}$, $r_3 = \frac{n_2 - n_3}{n_2 + n_3}$ are the relative indices of refraction. n_0, n_1, n_2 and n_3 are, respectively, the wavelength-dependent complex refractive indices of air, $MoSe_2$, SiO_2 and Si,

$$n_i = \mathrm{Re}(n_i) + \mathrm{Im}(n_i) \tag{4}$$

where $\mathrm{Re}(n_i)$ is the optical refractive index and $-\mathrm{Im}(n_i)$ is the absorption coefficient ($i = 0$, 1, 2, or 3). For n_0 (air) and n_2 (SiO_2), only the real part of the refractive index was used in the model. $\delta_1 = 2\pi d_1 n_1/\lambda$ and $\delta_2 = 2\pi d_2 n_2/\lambda$ are the phase shifts when light passes through $MoSe_2$ and SiO_2, respectively. $d = N \times d_1$ is the thickness of the $MoSe_2$ nanosheet, where N is the number of layers, d_1 is the thickness of single $MoSe_2$ layer, and d_2 is the thickness of the SiO_2 layer.

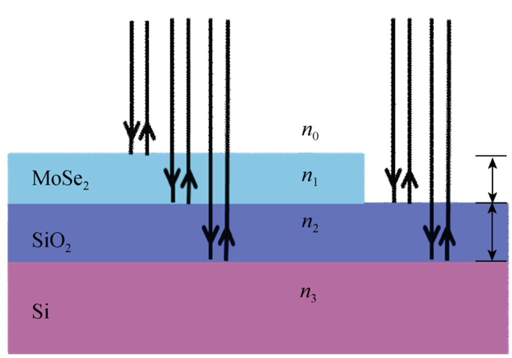

Fig. 1 Schematic depiction of light reflection in three-layered Fresnel's law model

3 Results and discussion

Figure 2 shows the color plots of the calculated single-layer $MoSe_2$ optical contrast on SiO_2/Si as a function of incident light wavelength with SiO_2 thickness ranging from 0 to 350 nm on Si substrate. From the calculations, it is clear that there are two bands with high, positive contrast for visible light with SiO_2 thickness of less than 350 nm. And the two bands with high contrast correspond to the thickness of SiO_2 in the range of 50–130 and 170–350 nm roughly. Considering that the red light and the green light are the major part when calculating the contrast, the silicon wafer around 90 and 275 nm should give the largest change of contrast. So, 275-nm SiO_2/Si substrates were selected in this experiment.

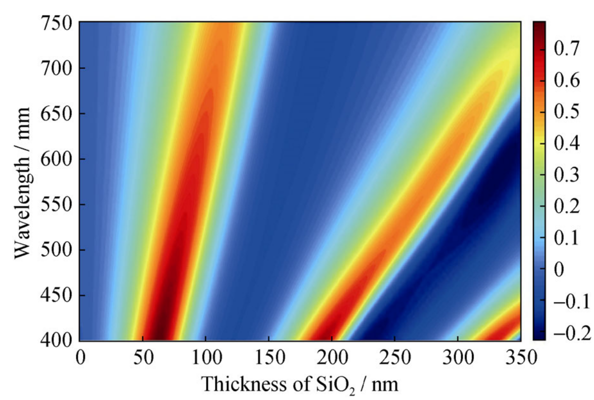

Fig. 2 Color plot of calculated optical contrast as a function of incident light wavelength from 400 to 750 nm and thickness of SiO_2 from 0 to 350 nm for single $MoSe_2$ nanosheet. Color bar representing optical contrast

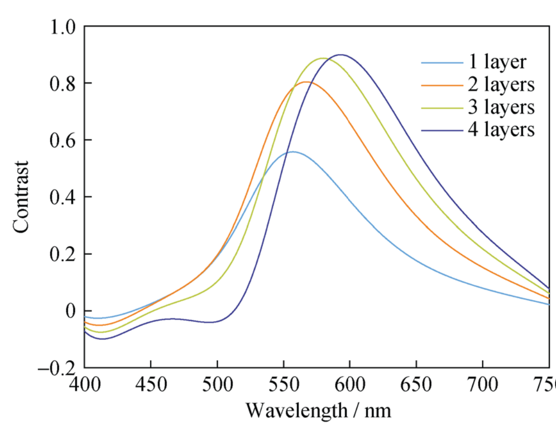

Fig. 3 Theoretically calculated optical contrast of 1- to 4-layer $MoSe_2$ nanosheets as a function of incident light wavelength on SiO_2 (275 nm)/Si substrate

Figure 3 gives the theoretically calculated results of optical contrast spectra of $MoSe_2$ nanosheet with various atomic planes on SiO_2 (275 nm)/Si substrate. It is clear that the contrast value changes a lot along the incident light wavelength, depending on the number of $MoSe_2$ layers, and the most obvious contrast is in the range of green light wavelength. The integration of the contrast values in visible light regions is performed. The average contrast values of 1- to 4-layer $MoSe_2$ are 0.22, 0.33, 0.36 and 0.34, respectively, given by the integrated value divided by the visible light range. It makes the identification of the $MoSe_2$ thickness possible that the contrast value depends on the number of $MoSe_2$ layers.

To determine the relation between the spectra contrast and the thickness of the $MoSe_2$ nanosheet, natural $MoSe_2$ crystals with different layers were exfoliated mechanically and transferred onto the freshly cleaned 275-nm-thick SiO_2-coated Si substrates. The optical images of the $MoSe_2$ nanosheet were captured at the exposure time of 80 ms by a Nikon MM-400 optical microscopy (OM). Figure 4a shows the surface image of a $MoSe_2$ nanosheet using an OM equipped with a color camera. Then, the sample was imaged using a BRUKER Dimension Icon atomic force microscopy (AFM) to measure the accurate thickness of the $MoSe_2$ nanosheet. Figure 4b, c is the corresponding 2D AFM images of the areas marked by white rectangles in Fig. 4a. The height values measured from the white solid lines (labeled as 1, 2 3, 4) in Fig. 4b, c are 0.72, 1.46, 2.23 and 2.88 nm (Fig. 5a$_1$–a$_4$), respectively, and the thickness of single $MoSe_2$ layer is about 0.72 nm. The thickness value is consistent with that reported by others [19]. These height values obtained in the samples correspond to 1- to 4-layer $MoSe_2$ nanosheets, respectively. Figure 5b$_1$–b$_4$ is the contrast profile of the yellow dashed rectangles highlighted in Fig. 4b, c generated by Image software. The contrast values of the 1- to 4-layer $MoSe_2$ nanosheets are 0.24, 0.33, 0.38 and 0.35, respectively. In addition to AFM, the spectrum of $MoSe_2$ nanosheets (1–4 layers) was also measured by spectroscopic ellipsometer (Horiba Uvisel FUV) under normal white light illumination. The optical spectra of 1- to 4-layer $MoSe_2$ of different illuminated wavelength fit well with the theoretically calculated results shown in Fig. 3.

Knowing the accurate thickness of the $MoSe_2$ nanosheet, it is able to make a correspondence with the optical contrast values. Figure 6 shows that the contrast of the theoretical calculation and experimental data changes with the number of $MoSe_2$ nanosheet layers. The calculated

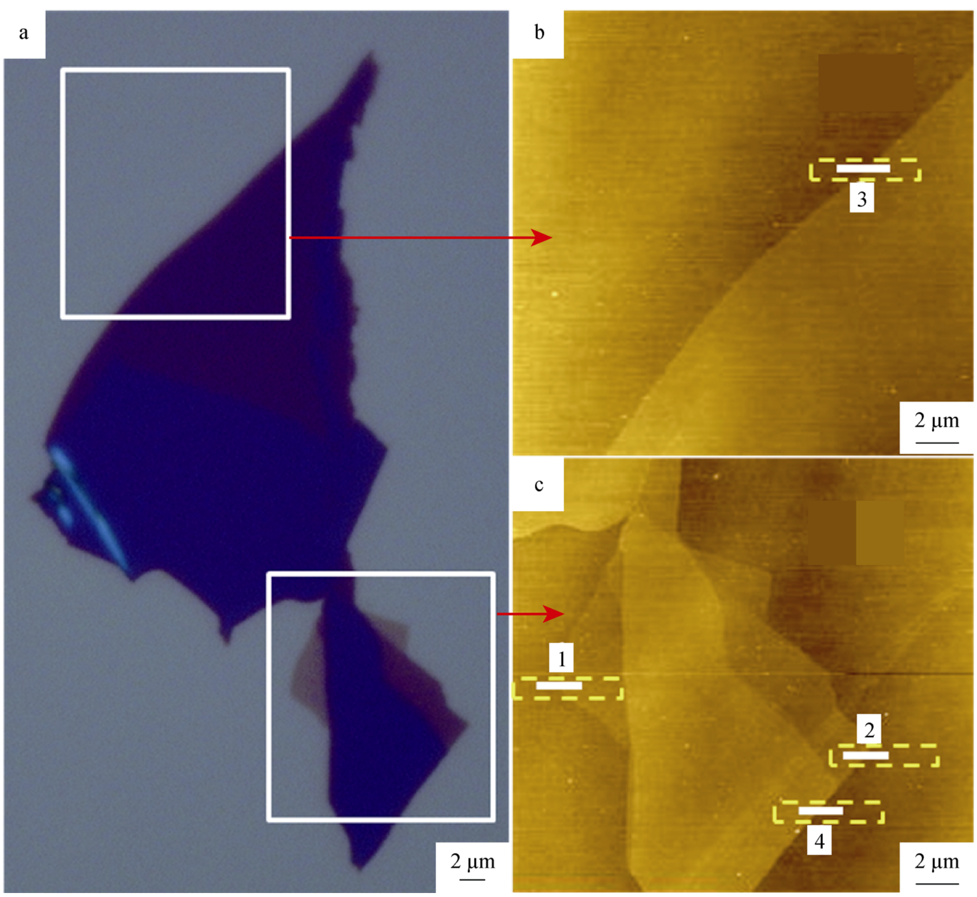

Fig. 4 OM image of 1- to 4-layer $MoSe_2$ nanosheets on SiO_2 (275 nm)/Si substrate **a** and corresponding 2D AFM images of selected areas **b**, **c**

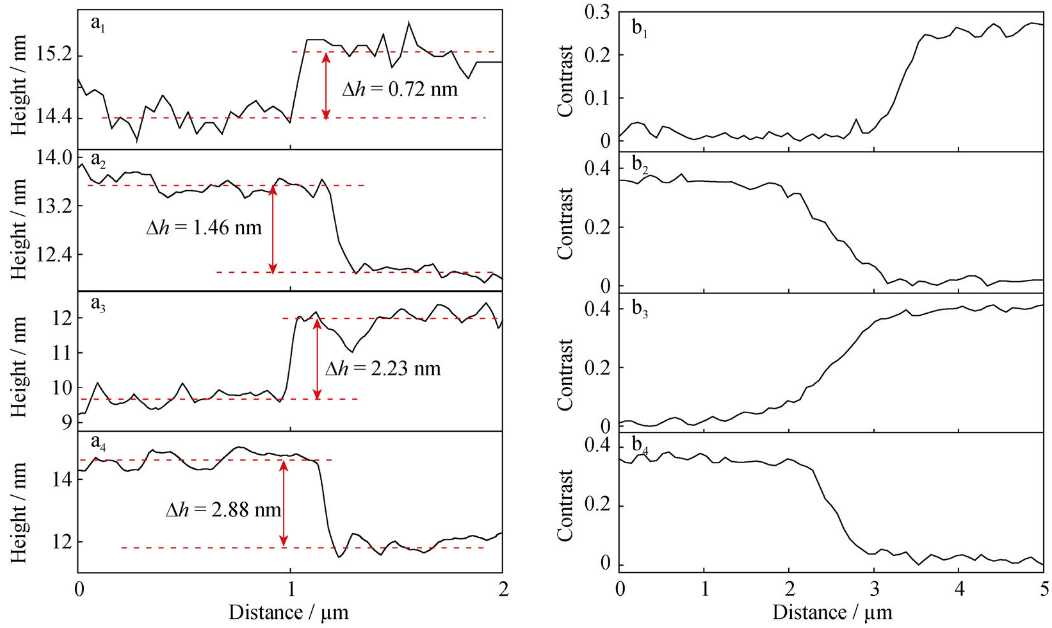

Fig. 5 Height profiles across white $\mathbf{a_1}$ solid Line 1, $\mathbf{a_2}$ solid Line 2, $\mathbf{a_3}$ solid Line 3 and $\mathbf{a_4}$ solid Line 4 (Δh being height difference of different layers) marked in Fig. 4b, c and contrast values of yellow $\mathbf{b_1}$ dashed Rectangle 1, $\mathbf{b_2}$ dashed Rectangle 2, $\mathbf{b_3}$ dashed Rectangle 3 and $\mathbf{b_4}$ dashed Rectangle 4 marked in Fig. 4b, c

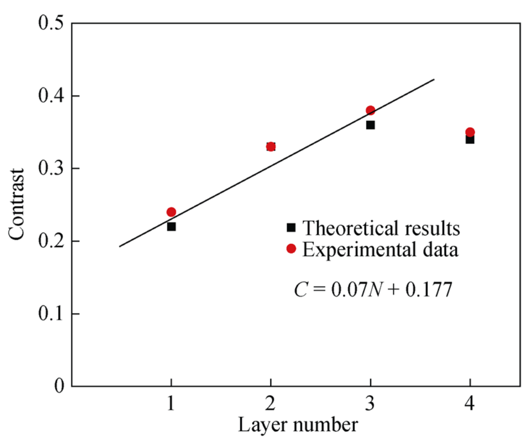

Fig. 6 Theoretical and experimental contrast (C) values as a function of $MoSe_2$ layer number (N)

optical contrast fits the contrast analyzed from OM pictures very well. In addition, for the layer number of less than 3, contrast values can be fitted as $C = 0.07N + 0.177$. One can see that the contrast linearly increases with $MoSe_2$ layer number increasing, making the identification of $MoSe_2$ thickness by OM possible.

4 Conclusion

The contrast of different layers $MoSe_2$ on 275 nm SiO_2/Si was calculated, and the theoretical calculation was verified by AFM and spectroscopic ellipsometer. The results show that the contrast values acquired by OM are consistent with the theoretically calculated contrast values, leading to identifing the thickness of $MoSe_2$ nanosheet accurately and rapidly possible. This work establishes a quantitative framework for detecting single and multiple layers of $MoSe_2$ and other 2D atomic crystals on top of various substrates. It is hoped to provide a lot of convenience on identifying the thickness of 2D materials in fundamental research and applications.

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References

[1] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA. Electric field effect in atomically thin carbon films. Science. 2004;306(5696):666.

[2] Geim AK, Novoselov KS. The rise of graphene. Nat Mater. 2007;6(3):183.

[3] Neto AHC, Guinea F, Peres NMR, Novoselov KS, Geim AK. The electronic properties of graphene. Rev Mod Phys. 2009; 81(1):109.

[4] Lee C, Yan H, Brus LE, Heinz TF, Hone J, Ryu S. Anomalous lattice vibrations of single- and few-layer MoS_2. ACS Nano. 2010;4(5):2695.

[5] Sun JF, Cheng F. Spin and valley transport in monolayers of MoS_2. J Appl Phys. 2014;115(13):133703.

[6] Nath M, Govindaraj A, Rao CNR. Simple synthesis of MoS_2 and WS_2 nanotubes. Adv Mater. 2001;13(4):283.
[7] Matte HS, Gomathi A, Manna AK, Late DJ, Datta R, Pati SK, Rao CN. MoS_2 and WS_2 analogues of graphene. Angew Chem. 2010;49(24):4059.
[8] Huang CM, Wu SF, Sanchez AM, Peters JJP, Beanland R, Ross JS, Rivera P, Yao W, Cobden DH, Xu XD. Lateral heterojunctions within monolayer $MoSe_2$–WSe_2 semiconductors. Nat Mater. 2014;13(12):1096.
[9] Zhang HM, He XB, Qu XH, Liu Q, Shen XY. Microstructure and thermal properties of copper matrix composites reinforced with titanium-coated graphite fibers. Rare Met. 2013;32(1):75.
[10] Xu HT, He DW, Fu M, Wang WS, Wu HP, Wang YS. Optical identification of MoS_2/graphene heterostructure on SiO_2/Si substrate. Opt Express. 2014;22(13):15969.
[11] Tongay S, Zhou J, Ataca C, Lo K, Matthews TS, Li JB, Grossman JC, Wu JQ. Thermally driven crossover from indirect toward direct bandgap in 2D semiconductors: $MoSe_2$ versus MoS_2. Nano Lett. 2012;12(11):5576.
[12] Ni ZJ, Wang YY, Yu T, Shen ZX. Raman spectroscopy and imaging of graphene. Nano Res. 2008;1(4):273.
[13] Meyer JC, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, Piscanec S, Jiang D, Novoselov KS, Roth S, Geim AK, Ferrari AC. Raman spectrum of graphene and graphene layers. Phys Rev Lett. 2006;97(18):187401.
[14] Koh YK, Bae M-H, Cahill DG, Pop E. Reliably counting atomic planes of few-layer graphene ($n > 4$). ACS Nano. 2011;5(1):269.
[15] Wang XF, Zhao M, Nolte DD. Optical contrast and clarity of graphene on an arbitrary substrate. Appl Phys Lett. 2009;95(8):81102.
[16] Li H, Lu G, Yin ZY, He QY, Li H, Zhang Q, Zhang H. Optical identification of single- and few-layer MoS_2 sheets. Small. 2012;8(5):682.
[17] Li H, Wu J, Huang X, Lu G, Yang J, Lu X, Xiong QH, Zhang H. Rapid and reliable thickness identification of two-dimensional nanosheets using optical microscopy. ACS Nano. 2013;7(11):10344.
[18] Blake P, Hill EW, Castro NAH, Novoselov KS, Jiang D, Yang R, Booth TJ, Geim AK. Making graphene visible. Appl Phys Lett. 2007;91(6):63124.
[19] Shaw JC, Zhou HL, Chen Y, Weiss NO, Liu Y, Huang Y, Duan XF. Chemical vapor deposition growth of monolayer $MoSe_2$ nanosheets. Nano Res. 2014;7(4):511.