Optical identification of few layers of MoS_2, $MoSe_2$, WS_2 and WSe_2

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We propose a study to identify mono- and few-layers of molybdenum disulfide, molybdenum diselenide, tungsten disulfide, and tungsten diselenide. The number of layers is determined by optical microscopy. The single and few layers of the transition metal dichalcogenides transferred onto SiO_2/Si substrates. SiO_2/Si substrates with 270 nm thickness SiO_2 have been shown to provide high optical contrast, enabling optical identification of the transition metal dichalcogenides easier.

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INTRODUCTION

After the rediscovery of graphene by A. Geim and K.Novoselov in 2004 with use of so-called called "Scotch tape method" [1], the mechanical exfoliation method has established to be as one of the powerful tool to isolate two-dimensional material from bulk layered crystal [2]. Many efforts have made on the development of easy methods to identify thin flakes. These based on the observation of the apparent color when they are transferred onto a SiO_2/Si surface. On this substrate, there is a dependency of the apparent color of the flake with its thickness due to thin-film interference effects have been developed to identify 2D materials and to determine their number of layers [3-4].

Optical microscopy is decided as a reliable and non-destructive method identifying the atomically thin and thick layers. This technique is valid for the less thickness of 2D materials. They can be observed through an optical microscope, because of the wavelength dependent reflectivity of the dielectric/2D material system [2]. This dependence can be exploited to easily identify and isolate 2D material single layer flakes by modifying the substrate dielectric thickness and permittivity. In addition to increasing the visibility, the use of different substrate materials may improve the performance of the produced devices if the chosen substrate has good dielectric properties [5–7].

In this work, we study the visibility of several 2D materials, such as MoS_2, $MoSe_2$, WS_2 and WSe_2. We explore the use of silicon dioxide (Si2O), which is almost exclusively used nowadays to fabricate nanodevices based on 2D materials. We show how the use of 285 nm of SiO_2 spacer layer (the standard in graphene and MoS_2 research nowadays) has its maximum contrast value at 460 nm, in the deep-blue/violet part of the visible spectrum.

EXPERIMENTAL PART

MoS_2, $MoSe_2$, WS_2 and WSe_2 samples were prepared out of a synthetic bulk crystals grown by vapor transport method (Graphene Supermarket, USA and 2D materials, Shanghai, China). First, we mechanically exfoliate bulk MoS_2, $MoSe_2$, WS_2 and WSe_2 using adhesive Scotch tape. These cleaved thin flakes on Scotch tape are deposited on a target substrate and rubbed by cotton stick to further cleave them. Subsequently, the flakes are transferred onto two different silicon substrates: one with a 285 nm thick SiO_2 oxide layer on top and another one with a 75 nm thick Si_3N_4 layer. The latter thickness was chosen after the theoretical

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analysis in order to maximize the contrast at a wavelength of 550 nm [9]. After the Scotch tape is removed, 1L and multilayer MoS_2, $MoSe_2$, WS_2 and WSe_2 are left on the substrate.

Few layer flakes are examined under an optical microscope (Nikon Eclipse LV100) and the number of layers of MoS_2 is determined by a combination of quantitative optical microscopy and atomic force microscopy. Here, contact mode atomic force microscopy used instead of tapping mode to avoid artifacts in the thickness determination. The number of layers of $MoSe_2$, WS_2 and WSe_2 has been defined by quantitative optical microscopy.

RESULTS AND DISCUSSION

In order to evaluate the potential of SiO_2 to enhance the optical visibility of 2D semiconductors we have first calculated the optical contrast of monolayer MoS_2, $MoSe_2$, WS_2 and WSe_2 as function of the illumination wavelength for substrates with SiO_2 layer of different thickness. The model is based on the Fresnel law and more details can be found in the literature [2,5]. Briefly, the optical contrast of atomically thin materials is due to a combination of interference between the reflection paths that originate from the interfaces between the different media and thickness dependent transparency of the 2D material that strongly modulates the relative amplitude of the different reflection paths. These two effects combined lead to color shifts (dependent on the thickness of the 2D material) that can be appreciated by eye.

The 2D nanolayer is modeled as a thin homogeneous film of thickness d1 with complex refractive index n1, where $Re(n_1)$ is the optical refractive index and $-Im(n_1)$ is the absorption coefficient. Previously published values for the refractive indices and absorption coefficients of bulk MoS_2, $MoSe_2$, WS_2 and WSe_2 are available in the literature [8–10]. The SiO_2 layer of thickness d_2 is optically characterized by a wavelength-dependent refractive index n_2 (λ) with only a real part [20], ranging from 1.47 at 400 nm to 1.455 at 700 nm. As the thickness of the Si layer (525 μm) is several orders of magnitude larger than the corresponding skin depth, it can be considered as a semi-infinite film. For visible light incidence, the intensity of reflected light from the stacking of two thin films on top of a semi-infinite layer is given by [11]

$$R(n_1)=\left|\frac{r_1e^{i(\phi_1+\phi_2)}+r_2e^{-i(\phi_1-\phi_2)}+r_3e^{-i(\phi_1+\phi_2)}+r_1r_2r_3e^{i(\phi_1-\phi_2)}}{e^{i(\phi_1+\phi_2)}+r_1r_2e^{-i(\phi_1-\phi_2)}+r_1r_3e^{-i(\phi_1+\phi_2)}+r_2r_3e^{i(\phi_1-\phi_2)}}\right|^2 \quad (1)$$

where

$$r_1=\frac{n_0-n_1}{n_0+n_1},\ r_2=\frac{n_1-n_2}{n_1+n_2},\ r_3=\frac{n_2-n_3}{n_2+n_3} \quad (2)$$

are the relative indices of refraction and $\phi_i=\frac{2\pi d_i n_i}{\lambda}$ are the phase shifts induced by changes in the optical path.

The visibility of the TMDC films is characterized in terms of the Michelson contrast [12]

$$Contrast=\frac{R_{mat}-R_{SiO_2}}{R_{mat}+R_{SiO_2}}, \quad (1)$$

where R_{mat} is the reflected intensity with the material and R_{SiO_2} is the intensity without the material. If the value of the contrast is zero, the material is not detectable; if the value is between 0 and -1, the material appears darker than the substrate; and if it is between 0 and +1, the material is brighter than the substrate.

In order to determine optimal conditions for the optical detection of nanolayers we used results from Benameur et all [13]. For all four materials and SiO_2 thickness lower than 300 nm, the contrast for visible light wavelengths exhibits two characteristic bands with high, positive contrast and one band with negative contrast. The two bands with positive contrast roughly correspond to SiO_2 thickness in the 50–100 nm and 200–300 nm range, implying that dichalcogenide nanolayers should, in principle, be visible on substrates with such oxide thicknesses for at least some spectral ranges of the visible light.

Results from quantitative optical microscopy and tapping mode AFM are shown in Figures 1 to 3. Here, single to five-layer (5L) MoS_2, $MoSe_2$, WS_2 and WSe_2 nanosheets with clean surfaces were deposited on Si substrates with 270 nm SiO_2 coating layer. AFM measurement indicates that the heights of 1L to 5L of MoS_2, $MoSe_2$ and WSe_2 nanosheets are 0.8(MoS_2), 2.9, 4.0 ($MoSe_2$), 1.7, 2.8, 3.6 (WSe_2) nm, respectively. In the case of WS_2 we couldn't image AFM for thinner flakes.

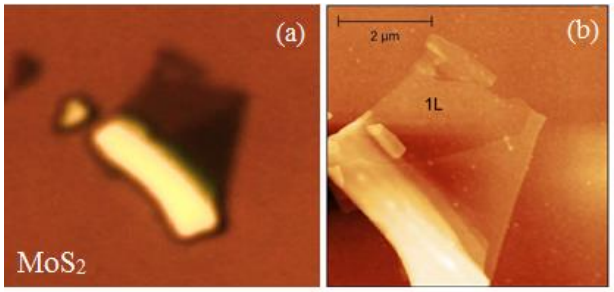

Figure 1. Contrast map of a MoS_2 flake deposited onto a 270 nm SiO_2/Si substrate under illumination with visible light; (b) Topographic atomic force microscopy image.

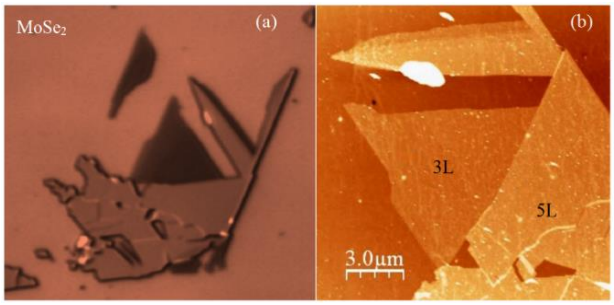

Figure 2. Optical and AFM images of MoS_2 nanolayers deposited on 270 nm SiO_2 with corresponding contrast and height.

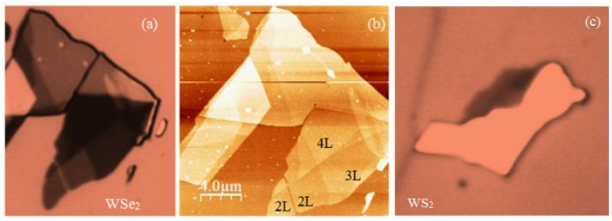

Figure 3. Multilayered WSe_2 flake (a) and WS_2 (b) deposited on a 270 nm SiO_2/Si surface.

CONCLUSION

To summarize, we have obtained single and few layers of MoS_2, $MoSe_2$, WS_2 and WSe_2. Mechanical exfoliation followed by optical and AFM imaging has confirmed that single and multilayer dichalcogenide nanostructures can be visualized on substrates with proposed oxide thicknesses with easy differentiation between structures containing single to few layers. Optical imaging can therefore be used as a simple, non-destructive and low cost method for the detection of dichalcogenide few layers. Further studies will going on with use of different substrate material.

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REFERENCES

[1] Novoselov, K. S.; Geim, A. K.; Morozov, S. V; Jiang, D.; Zhang, Y.; Dubonos, S. V; Grigorieva, I. V; Firsov, A. A. Electric field effect in atomically thin carbon films. Science 2004, 306, 666–669.

[2] Blake, P.; Hill, E.W.; Castro Neto, A.H.; Novoselov, K.S.; Jiang, D.; Yang, R.; Booth, T.J.; Geim, A.K. Making graphene visible. Appl. Phys. Lett. 2007, 91, doi:10.1063/1.2768624.

[3] Ni, Z. H.; Wang, H. M.; Kasim, J.; Fan, H. M.; Yu, T.; Wu, Y. H.; Feng, Y. P.; Shen, Z. X. Graphene thickness determination using reflection and contrast spectroscopy. Nano Lett. 2007, 7, 2758–2763.

[4] Jung, I.; Pelton. M.; Piner, R.; Dikin, D. A.; Stankovich, S.; Watcharotone, S.; Hausner, M.; Ruoff, R. S. Simple approach for high-contrast optical imaging and characterization of graphene-based sheets. Nano Lett. 2007, 7, 3569–3575.

[5] Abergel, D.S.L.; Russell, A.; Fal’ko, V.I. Visibility of graphene flakes on a dielectric substrate. Appl. Phys. Lett. 2007, 91, 063125.

[6] Casiraghi, C.; Hartschuh, A.; Lidorikis, E.; Qian, H.; Harutyunyan, H.; Gokus, T.; Novoselov, K.S.; Ferrari, A.C. Rayleigh imaging of graphene and graphene layers. Nano Lett. 2007, 7, 2711–2717.

[7] Roddaro, S.; Pingue, P.; Piazza, V.; Pellegrini, V.; Beltram, F. The optical visibility of graphene: Interference colors of ultrathin graphite on SiO2. Nano Lett. 2007, 7, 2707–2710.

[8] Beal A R and Hughes H P 1979 J. Phys. C: Solid State Phys.12. 881.

[9] Beal A R, Liang W Y and Hughes H P 1976 J. Phys. C: Solid State Phys. 89. 2449.

[10] Beal A R, Hughes H P and Liang W Y 1975 J. Phys. C: Solid State Phys. 8. 4236.

[11] Blake P et al 2007 Appl. Phys. Lett. 91. 063124.

[12] Li, H.; Wu, J.; Huang, X.; Lu, G.; Yang, J.; Lu, X.; Xiong, Q.; Zhang, H. Rapid and reliable thickness identification of two-dimensional nanosheets using optical microscopy. ACS Nano 2013, 7, 10344–10353.

[13] M.M. Benameur, B. Radisavljevic, J.S. Heron, S. Sahoo, H. Berger and A. Kis. Visibility of dichalcogenide nanolayers. Nanotechnology 22 (2011) 125706. doi. 10.1088/0957-4484/22/12/125706.