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Confocal Microscope Studies of MoS_2 Layer Thickness

M. Grzeszczyk, K. Gołasa, B. Piętka, A. Babiński and J. Szczytko
Nanostructures Engineering, Institute of Experimental Physics, Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warszawa, Poland

We have been studying micro-luminescence of various exfoliated MoS_2 flakes using a confocal microscope. A crucial issue is to determine thickness of the investigated layer. The common way — using atomic force microscopy, electron microscopy or the Raman spectroscopy — requires moving the sample out from the confocal microscope experimental setup and looking for a particular exfoliated flake hidden among thousands of others. In order to preliminarily determine thickness of investigated layers we have performed a study on optical reflectivity and compared the results with the Raman spectroscopy investigations. In this way we were able to calibrate our experimental setup. Optical measurements are much faster than the Raman spectroscopy and can give a good estimation of MoS_2 thickness.

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1. Introduction

Layered transition metal dichalcogenides MX_2 (where M = transition metal, X = S, Se) in two-dimensional structure reveal unique physical and optical properties. A typical example of this type of compounds is molybdenum disulfide (MoS_2), a naturally occurring mineral, whose structure is characterized by strong ion-covalent bonds between atom layers of sulfur and molybdenum and by weak van der Waals bonds between S–Mo–S layers [1]. Molybdenum disulfide is a well-known semiconductor, that in its two-dimensional form has interesting properties, such as, for example, a direct energy band gap of 1.87 eV (while the bulk is an indirect-gap semiconductor with a band gap of about 1.3 eV). Potential application of MoS_2 reaches the fields from electronics to energy storage [2], photovoltaic [3] and photocatalytic applications [4]. Several applications of monolayer MoS_2 have recently been proposed in logical circuits [5], field effect transistors [6] and optoelectronics [7]. One of methods of MoS_2 single-layer crystal preparation is mechanical exfoliation [8] from molybdenite which is based on delamination of the material volume with an adhesive dicing tape. However, exfoliated samples contain flakes of different size and thickness. In order to estimate the crystals' thicknesses the method of optical contrast measurements was proposed by Castellanos-Gomez et al. [9].

In this paper we compare this approach with the Raman spectroscopy measurements. We show a method to estimate the thickness of investigated sample by optical contrast in a quick and convenient way.

2. Experiment

The samples were prepared by mechanical exfoliation using molybdenite from Molly Hill deposit in Canada on a Si/75 nm SiO_2 substrate. An Attocube confocal microscope (CFM) was used for scanning the surface of the samples. The measurement was carried out in the standard pressure and room temperature. Two separated optical paths allowed us to simultaneously investigate two outputs: a reflection beam and photoluminescence (schematic of the setup is shown in Fig. 1a). Experimental setup allowed for the spatial resolution up to about 300 nm with the continuous wave 532 nm green laser light. We used 50× magnification achromatic objective of 0.82 NA and 0.4 mm working distance.

Micro-Raman spectroscopy was performed using Nd:YAG laser with wavelength of 532 nm. The spatial resolution was 3 μm.

3. Results

The Raman spectra reveal characteristic resonances of MoS_2, which are assigned to E^1_{2g} and A_{1g} vibrational modes [10]. The energy difference between E^1_{2g} and A_{1g} changes with the thickness of the sample — from about 25 cm^{-1} for bulk material to 19 cm^{-1} for single MoS_2 monolayer [1]. We used micro-Raman spectroscopy to get information about the thickness of our MoS_2 flakes (Fig. 1b). The Raman spectrum was recorded with excitation spots of 3 μm size. Afterwards the sample was placed in a confocal microscope, the same piece of crystal (previously measured by the Raman spectroscopy) was found and the reflectivity map was recorded (inset in Fig. 1b).

4. Discussion

The reflectivity of MoS_2 flakes taken with CFM was compared with results of the Raman spectroscopy (Fig. 1b). The correlation between the number of monolayers and the intensity of reflected light can be used for a preliminary determination of the thickness of exfoliated flakes [9]. The energy difference between E^1_{2g} and A_{1g} is directly proportional to a thickness of measured layer. From the intensity of reflected light the relative reflectivity R_R was calculated as: $R_R = \frac{I_{MoS_2}}{I_{Si/SiO_2}}$ where I_{MoS_2} denotes the intensity of the light reflected from MoS_2 collected at each position on the sample measured previously by the Raman spectroscopy, and the light reflected from Si/SiO_2 collected at any position on the substrate. The background level was determined in each experiment

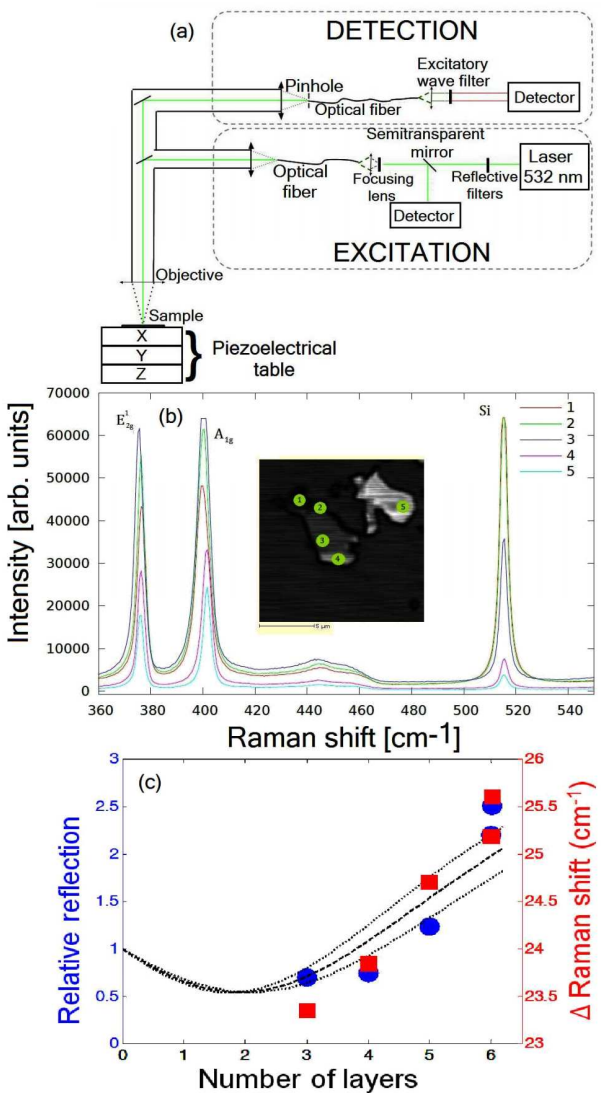

Fig. 1. (a) Scheme of confocal microscopic measurement setup. (b) The reflectivity of MoS_2 flakes (inset) compared to results of the Raman spectroscopy. The different positions from which the Raman spectra were taken are marked by circles. Characteristic resonances from Si substrate and E^1_{2g}, A_{1g} modes of MoS_2 are marked. (c) The comparison of relative reflection (R_R, circles, left axis), the energy difference between E^1_{2g} and A_{1g} (Δ Raman shift, squares, right axis) and the thickness of the MoS_2 flakes. Transfer matrix calculations are presented by black lines for $n = 6.4$ (upper dotted line), $n = 6.1$ (middle dashed line), $n = 5.8$ (lower dotted line).

as the darkest spot in the recorded image and was subtracted from both intensity values. The results of relative reflection R_R are compared with the Raman shift difference and they show the same tendency, as illustrated in Fig. 1c.

Transfer matrix method was used to calculate the reflectivity of exfoliated MoS_2 flakes deposited on Si/SiO_2 substrate. The thickness of SiO_2 was 75 nm. The calculations were performed for the wavelength of 532 nm with known values of refraction indexes of SiO_2 and Si from Ioffe Physical Technical Institute database. Optical length nd of MoS_2 was fitted (n — refraction index, d — thickness). With the assumption that the thickness of MoS_2 single layer is $d = 0.65$ nm [6], one can estimate the value of refractive index. According to our fit it is $n = 6.1 \pm 0.3$. Using only one wavelength we were able to fit only real part of n. The value of n we obtained slightly differs from the estimations by Castellanos-Gomez et al. (2010) [9]. In the cited paper the authors used $d = 0.54$ nm, thus estimated $n = 7$ for 532 nm. In our case, the value for $d = 0.54$ nm would give $n = 7.3$. However, if we use estimated in paper [9] imaginary value of complex index of refraction $\kappa = 1.7$ we did not obtain a reasonable fit to our data. This discrepancy needs to be addressed in future work with measurement performed at different wavelengths. Nevertheless, optical contrast gives possibility to estimate the thickness of MoS_2 with the precision of one monolayer (see Fig. 1b).

3. Conclusions

The comparison between the Raman spectroscopy and reflectivity measurements allows for estimation of MoS_2 thickness with the precision of one monolayer. From the transfer matrix calculations fit to our experimental data we estimated the index of refraction of single MoS_2 layers of $n = 6.1 \pm 0.3$ for the single-layer thickness of $d = 6.5$ at the wavelength 523 nm.

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