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Excitonic nature of dispersion of two-dimensional transition metal dichalcogenides and effect of annealing on excitons

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Abstract. In present study, we develop an effective and universal technique for retrieving dispersion of bulk and monolayer TMDs from spectroscopic ellipsometry measurements. The basis of the method is excitonic nature of the dispersion. In addition, we demonstrate beneficial influence of annealing on optical properties of MoS_2.

1. Introduction

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have recently become the focus of many research works due to their outstanding electrical and optical properties [1-2], which make them suitable for a variety of different applications [1]. These materials have been already successfully used as a building block for solar cells [3], transistors [4], sensors [5], light emitters [6], transparent and conductive electrodes [7] and lasers [8], demonstrating the performance even higher than devices based on graphene [9]. With such a broad optoelectronic applications, it is vitally important to precisely know optical constants (ε_1 and ε_2) of TMDs.

To date, there are about 30 published works, dedicated to optical properties of TMDs. They have been characterized using a variety of optical techniques such as photoluminescence (PL) [10], absorbance [11], optical contrast reflectivity [12]. Among them the most sensitive and precise [13] for thin films is spectroscopic ellipsometry [14-16]. Although obtained results show similar behavior for dielectric function, the absolute values of ε_1 and ε_2 differs a lot (within 50 %). This occurs because of sensitivity of physical properties of TMDs to surroundings [17], defects [18] and synthesis method [19]. As a result, it is not clear which data should be used for calculation of theoretical performance of the devices based on TMDs.

To solve this problem we propose a universal algorithm for optical constants determination of 2D TMDs using spectroscopic ellipsometry (SE) and demonstrate it on the example of Chemical Vapor Deposition (CVD)-grown MoS_2, $MoSe_2$, WS_2 and WSe_2 as the most commonly used among others [1]. Analysis were carried out taking into account dominated contribution of excitons into dielectric function [2, 14] which has not been done before [14-16]. Therefore it could be potentially applied to the others TMDs because of similarity of physical properties [2]. Furthermore, for the first time we determine optical constants of 2D TMDs in near and medium infrared region (IR) and show that for these wavelengths $\varepsilon_2 = 0$ (no absorption) for all TMDs and ε_1 is higher than 12 for monolayer MoS_2, which makes it an ideal platform for waveguides for IR region [20]. Finally, we show that annealing helps to increase absorption for A and B-excitons due to reducing contaminations such as water which could be useful for improving performance of photodetectors and solar cells [9].

2. Experimental section

SE measurements were performed were performed on a variable-angle spectroscopic ellipsometer (VASE, J. A. Woollam Co.) in a broad wavelength range 300 – 3300 nm. Analysis were carried out taking into account excitonic nature of dispersion. In considering wavelength interval excitons originates from different interband transition. Therefore, they can be described by using Tauc-Lorentz oscillators [18], one for each exciton. For imaginary part of dielectric function for Tauc-Lorentz oscillator reads:

$$\varepsilon_2 = \begin{cases} \dfrac{AE_0C\left(E-E_g\right)^2}{(E^2-E_0^2)^2+C^2E^2}\dfrac{1}{E} & for\ E > E_g \\ 0 & for\ E \leq E_g \end{cases}$$

, where A - oscillator strength, C - broadening of the peak, E - photon energy, E_g - optical band gap, E_0 - peak central energy. The real part of the dielectric function is derived from the expression of imaginary part via Kramers-Kronig integration.

3. Results and discussion

Figure 1 shows obtained dielectric function for MoS_2 (6 Tauc-Lorentz oscillators) and WS_2 (5 Tauc-Lorentz oscillators). The advantage of such approach is each oscillator corresponds to one exciton and, as a result, its parameters reflect physical properties of excitons. For instance, critical points are equal to the positions of the maxima. For MoS_2 they were found to be at 1.83, 1.97 and 2.85 eV for A, B and C-excitons respectively, that is in a good agreement with the previously published work (1.88, 2.02 and 2.86 eV) [14]. In addition, suggested algorithm could be applied without changing to any TMDs with the excitonic nature of dispersion (ex. PtSe2, PtS2 and PdSe2). It is worth mention that in IR region MoS_2 does not have any absorption, while its real part is quite high ($\varepsilon_1 > 12$).

In order to improve optical properties of MoS_2 we annealed samples at 300 °C during 1 hour. The absorption of samples for A- and B-excitons increased after annealing as can be seen in Figure 2.

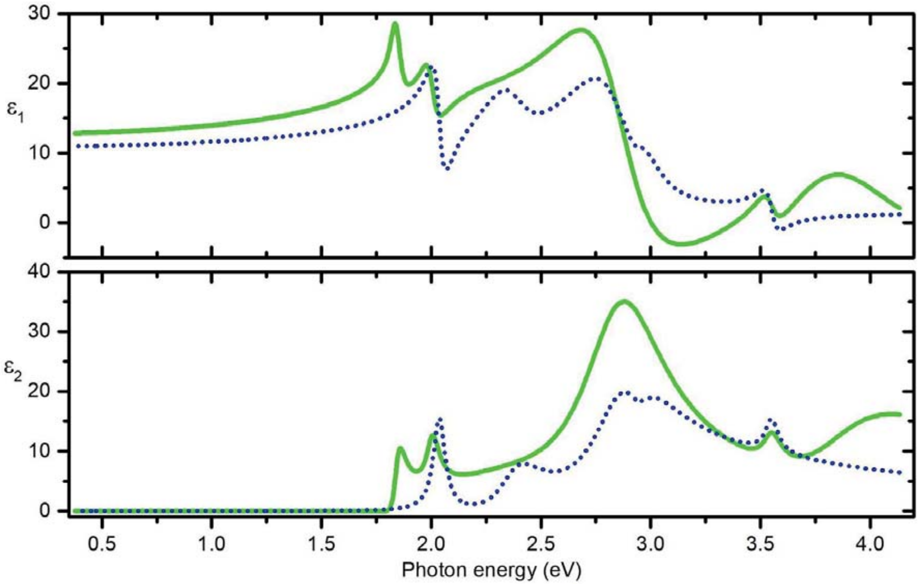

Figure 1. Dielectric function of monolayer MoS_2 (solid green line) and WS_2 (dotted blue line), obtained by fitting excitonic peaks using Tauc-Lorentz oscillators.

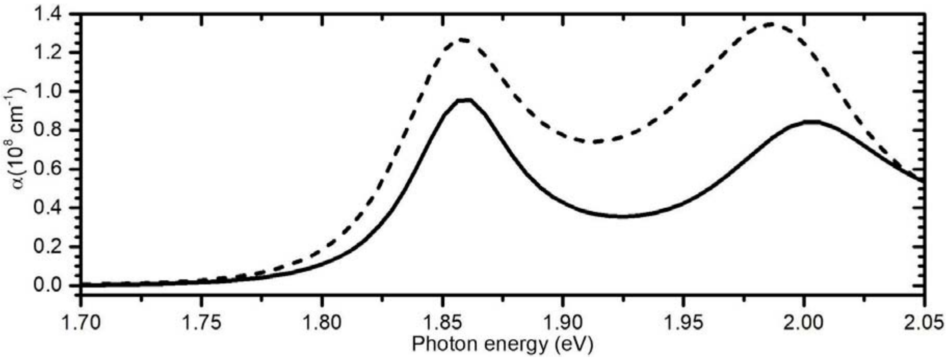

Figure 2. Absorption coefficient of MoS_2 for A- and B-excitons before (solid line) and after annealing (dashed line).

4. Conclusions

We developed an algorithm for finding dispersion of transition metal dichalcogenides. This technique is based on excitonic nature of dispersion and allows easily retrieving physical properties of excitons, for example, critical points. Furthermore, we demonstrated the influence of annealing on the optical properties of MoS_2, namely, an increase in the absorption of A- and B-excitons which is critical for applications.

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