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Exithon reflection spectra in thin layers WS_2

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The spectra of polarised light reflection from WS_2 multilayers deposited on a Si/SiO_2 substrate were investigated. It was shown that the features of the photoluminescence and reflection spectra at energies in the range of 1.9−2.1 eV are related to the dimensional quantisation of polaritons in a WS_2 layer with a thickness of 0.32 mkm. The parameters of exciton polaritons, such as resonance frequency, oscillator strength, and damping, were determined. When studying the spectral dependence of the circular polarisation of light reflected from the sample, optical anisotropy was observed.

Keywords: spectroscopy, transition metal dichalcogenides, polarisation, excitons.

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1. Introduction

Multilayer dichalcogenides of transition metals [1], such as WS_2, MoS_2 and others, are a class of materials with unique physical and chemical properties [2–4], which make them specifically attractive for use in nanoelectronics, optoelectronics and catalytical processes. These materials are characterized with two-dimensional structure, where atoms are arranged in a plane, and interlayer interactions are determined by poor Van der Waals attraction. As a result, the change in the number of layers in such systems causes considerable changes in their electron and optical characteristics, which makes them an object of intense studies [5–8].

Optical spectroscopy is an important tool to study multilayer dichalcogenides. These methods make it possible to research various aspects of materials, including their crystalline structure, electronic transitions, interaction between the layers and effects related to excitons. Depending on the number of layers, the properties of excitons may vary to a large extent, which opens new opportunities for design of optoelectronic devices. For example, due to the presence of pronounced peaks of exciton absorption in optical spectra of multi-layer dichalcogenides of transition metals, it becomes possible to design highly effective photodetectors and laser devices with improved sensitivity [9,10]. In the multi-layer structures, on the contrary, exciton effects may weaken, but exciton transport may appear perpendicularly to the layers.

Multi-layer dichalcogenides have unique properties, such as presence of direct and indirect exciton transition depending on the number of layers [5]. Monolayers usually demonstrate a direct transition, which causes high efficiency of light emission and absorption. In the multilayer structures the transition to the indirect transition may substantially change the optical characteristics, which has critical consequences for design of new optoelectronic devices.

Moire layers of dichalcogenides are of special interest, when adjacent layers turn towards each other at a certain angle [11,12]. This may cause appearance of moire quantum dots, effect of double refraction, and to linear and even circular dichroism [13,14].

This article studied multi-layers of dichalcogenide WS_2. Exciton parameters were defined in multilayers, such as oscillator force and exciton resonance energy. The phenomenon of light double refraction was found.

2. Experimental data

This paper studied the spectra of reflection from thin layers of tungsten disulfide (WS2), arranged on the substrates from oxidized silicon (Si/SiO_2). Structures were produced by the method of mechanical exfoliation of volume WS_2, and then the layers were transferred to the substrate Si/SiO_2. In process of exfoliation, one-ten monolayers WS_2 were separated from the bulk piece, which made it possible to make various thicknesses of layers (Figure 1).

It is important to note that the upper, finer layers could partially deviate from the lower ones, which caused increase of interlayer spacing for the upper layers compared to thicker ones. Besides, the exfoliation could lead to layers rotation towards each other at a small angle not exceeding one degree. Such rotation produces a moire structure, which may manifest itself in formation of lateral quantum dots [14], and may also cause optical anisotropy [15] and even optical activity [16].

Spectra of polarized reflection were measured at normal incidence of light at temperature 10 K. As a result, the spectral dependences of Stokes parameters for reflected light were obtained, including the degree of linear polarization (P_{lin}), the extent of circular polarization (P_{cir}) and

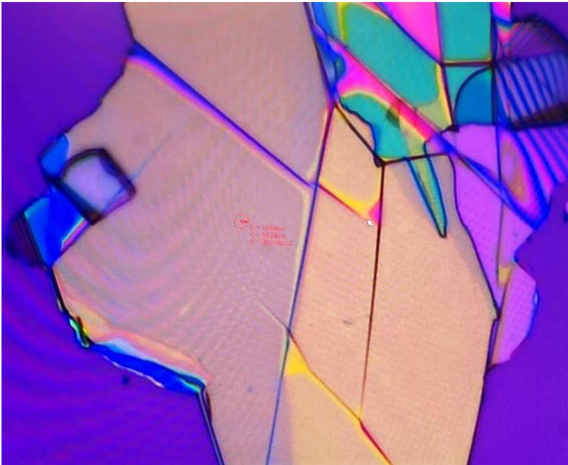

Figure 1. Photographic image of the surface of the WS_2 multilayer sample on an oxidized silicon substrate. Different colors correspond to different layer thicknesses. (Blue-purple — finer ones, compared to yellow-orange ones).

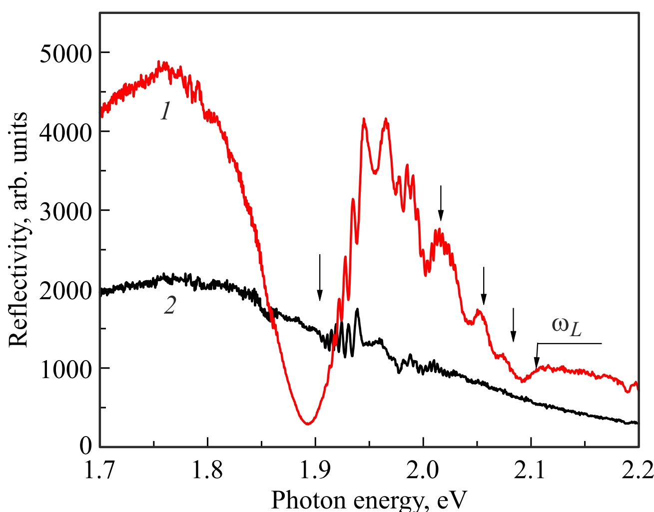

Figure 2. Reflection spectra recorded at temperature of 10 K, with normal incidence of light. Red curve (*1*) is taken off the multilayers WS_2 placed on the substrate. Black curve (*2*) is taken off the substrate from oxidized silicon. Arrows indicate the position of interference details. Symbol ω_L marks the longitudinal frequency of exciton.

the extent of linear polarization in the axes turned to 45° relative to the incident light polarization direction ($P_{\mathrm{lin}'}$).

The specimen was placed in a cryostat of closed cycle, which provided stable temperature conditions for experimenting. The source of light was a halogen lamp, the light of which used to focus on the specimen. The reflected signal was collected using a microscope, then moved through the diaphragm and was registered using spectrometer with focus distance 0.5 m and CCD detector. Selecting the size and position of the diaphragm, we could select the optimal points in the specimen to record the spectra, which made it possible to obtain precise and representative data.

Figure 2 presents spectra of reflection from multilayers WS_2, (curve *1*) and substrates Si/SiO_2 (curve *2*), obtained at normal incidence of light. Experimental data demonstrates the complex pattern of reflection spectrum caused by light interference both in layers WS_2, and in the substrate Si/SiO_2. Some of the observed features of the spectra of reflection from WS_2 match those that are observed for substrate Si/SiO_2, and are related to light interference in layer SiO_2. However, certain features are only observed in the spectrum WS_2.

Article [17] did benchmarking of these spectra, in process of which the thicknesses of layers SiO_2 and WS_2 were defined, and interference features were also identified, being related to both substrate Si/SiO_2 and WS_2. Specific features were found in the reflection spectrum WS_2, related to light interference near the exciton resonance. These features are indicated with arrows in Figure 2.

Knowing the positions of these features, you may restore the dispersion of the refractive index near the exciton resonance, as in the method described in paper [18]. As a result, the key parameters of exciton were determined in multi-layer WS_2, including energy of exciton resonance, value of longitudinal-transverse splitting and exciton decay. Figure 3 presents the dependence of light refractive index on energy of photons $n(\omega)$ in the area of exciton resonance, calculated with neglection of the space dispersion. Due to a weak bond between layers WS_2 you can neglect the exciton movement across the layers and not account for space dispersion and presence of additional waves [19]

$$n^2(\omega) = \varepsilon(\omega) = \varepsilon_0\left(1 + \frac{\omega_{LT}}{\omega_0 - \omega - i\Gamma}\right). \quad (1)$$

Here $\varepsilon(\omega)$ — dielectric permittivity considering the presence of exciton resonance, ε_0 — background dielectric permittivity at frequency of exciton resonance, $\hbar\omega_{LT}$ — value of longitudinal-transverse splitting, $\hbar\omega_0$ — energy of exciton resonance, $\hbar\Gamma$ — exciton decay.

Spectra of polarized reflection from these structures were also studied, and reflected light Stokes parameters were defined. It was found that when linearly polarized light is incident on the specimen, the reflected signal turned out to be polarized in a circle.

Degrees of circular polarization P_{cir}, reflected from the light specimen, are defined as follows:

$$P_{\mathrm{cir}}(\omega) = \frac{I_+(\omega) - I_-(\omega)}{I_+(\omega) + I_-(\omega)}.$$

Here $I_+(\omega)$, $I_-(\omega)$ — intensities of reflected light measured in the right and left circular polarizations.

It was found that the degree of circular polarization of the lines associated with reflection from WS_2, depends on the direction of incident light polarization relative to a certain axis in the specimen. In a certain direction of polarization, the polarization degree reaches the maximum value, when

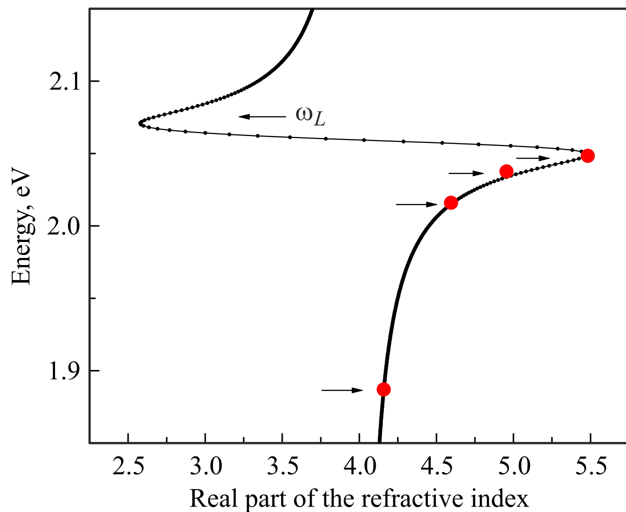

Figure 3. Dispersion of refractive index near the exciton resonance and position of interference features in the reflection spectrum in layer WS_2. Dots — experiment. Curve — calculation with parameters (energy of exciton resonance $\hbar\omega_0 = 2.06$ eV, background dielectric permittivity [20,21], value of longitudinal-transverse splitting $\hbar\omega_{LT} = 15$ meV [22], exciton decay $\hbar\Gamma = 10$ meV, thickness of layer WS_2 $d = 0.32\,\mu$). The values of the produced parameters demonstrate a good match to the data presented in previously published studies [22–24].

the polarization plane is turned by 45 degrees, it changes to zero, and when rotated by 90 degrees it changes its sign (Figure 4).

3. Results and discussion

We identify the features of the spectra of reflection from multilayers WS_2 as manifestation of dimensional quantization of exciton polaritons in thin crystalline wafers [18]. Knowing the wafer thickness [17], you can restore the polariton dispersion curves near the resonance energy. The exciton parameters obtained from the adjustment agree well with the literature data.

Appearance of the circular polarization in the reflection spectrum with the incidence of linearly polarized light onto the specimen indicates a birefringence phenomenon and the presence of an optical axis in this specimen.

The presence of the optical axis may be related to the formation of a moire pattern in multilayers WS_2. Mechanical splitting of a volume specimen of tungsten disulfide with the help of an adhesive tape: first of all, may cause increase in an interlayer spacing, second, to their displacement relative to each other both by the angle and in the plane when applied onto the substrate. These factors may manifest themselves in formation of an optical axis and cause birefringence.

4. Conclusion

The paper studied the spectra of polarized reflection from multilayers WS_2 placed onto Si/SiO_2 substrate. The conclusion of article [17] was confirmed that the features of photoluminescence and reflection spectra in the area of energies 1.9–2.1 eV were due to dimensional quantization of polaritons in a rather thin layer WS_2. The parameters of such exciton polaritons were defined, such as resonance frequency, oscillator force and decay. The produced values agree with the values from paper [22] for monolayers MoS_2.

Manifestation of optical anisotropy was found in the study of spectral dependence of circular polarization of the light reflected from the specimen.

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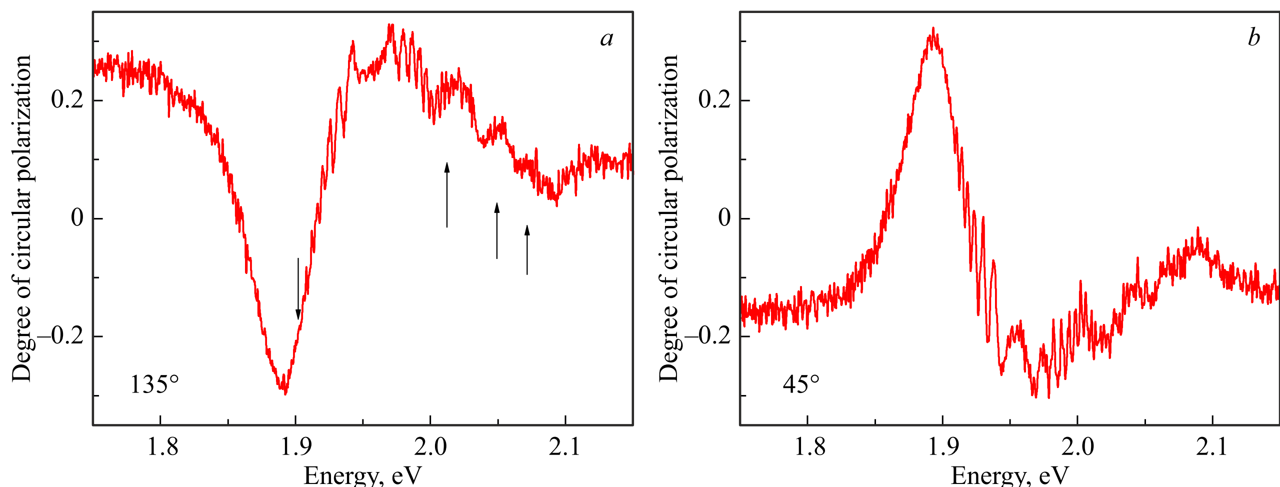

Figure 4. *a*) Extent of circular polarization of light reflected from the specimen and *b*) when the incident light polarization plane is rotated by 90°. Arrows indicate the features of the reflection spectrum inherent only in layer WS_2.

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Conflict of interest

The authors declare that they have no conflict of interest.

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