Long-lived photoinduced absorption in granular molybdenum disulfide thin films

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Abstract. We present results of the differential photoinduced absorption spectra investigation of the molybdenum disulfide nanogranular thin films. The films were produced by means of a sulfurization of pre-deposited by magnetron sputtering thin molybdenum films. It has been shown that photoexcitation with the light quanta with the energy higher than the bandgap leads to a modification of the absorption spectra in the visible range. Possible nature of the photoinduced absorption spectra will be discussed.

1. Introduction
Two-dimensional (2D) materials, especially single-layer ones, attracted a lot of attention in the recent time. It is due to the properties cannot be realized in the bulk. However, an absence of reproducible methods for synthesis of such kind of materials inhibited experimental developments. Successful synthesis of graphene drastically increased the interest to 2D materials. Two-dimensional transition metal dichalcogenides represent a special class among them. The use of these materials in nanoelectronic and optoelectronic devices is expected [1].

2. Experimental section
Molybdenum disulfide thin films have been prepared in two steps. At the first step, thin films of molybdenum were deposited by magnetron sputtering technique onto the fused silica and silicon substrates. Film thickness was measured at the edge between the film surface and undeposited region with Bruker DektakXT profilometer and had a value of ~4 nm. Then the films were annealed at 800°C in a weak flow of sulfur vapor (Figure 1). High purity argon gas (99.999%) has been used for a transport of sulfur.

Morphology of the produced thin film on silicon substrate was studied by scanning electron microscopy (Merlin, Carl Zeiss). Optical transmission of thin MoS$_2$ film on the fused silica substrate...
was investigated with the SPECORD M40 spectrophotometer (Carl Zeiss) at room temperature. Photoinduced absorption measurements were performed with an intent to study long-lived photoexcited states. Excitation (355 nm, 405 nm, 532 nm) was modulated by an optical chopper. Measurements have been carried out with different power and at different frequencies of the modulation.

3. Results and discussion

Scanning electron microscopy image of synthesized thin film of molybdenum disulfide on silicon substrate is shown in Figure 2a. Clearly, the sample is a nanogranular film composed of triangular, truncated-triangular, hexagonal and round-shaped flakes. Thickness of these flakes is about several nanometers, while longitudinal dimension is about 100 nm.

Figure 2. SEM image of the MoS$_2$ thin film on the silicon substrate (a); transmission spectrum of MoS$_2$ thin film on the fused silica substrate (b). The term corresponding to scattering processes is subtracted from the raw data in (b). Solid lines indicate the results of the spectrum fit with the sum of the two Voight components.

Optical transmission spectrum is presented in Figure 2b. It is clear that there are two absorption bands at 1.83 eV and 1.98 eV in the spectrum. These bands correspond to the well-known A and B exciton absorption lines, respectively [1]. Excitons are forming at the K and K’ points of the Brillouin zone split by the spin-orbit interaction. The absorption spectrum was fit with the sum of two Voight functions. It should be noted that positions of these bands depends on the thickness of the film [2].

In the simplest approximation, an exciton can be represented as a dipole consisting of an electron and a hole, which are held together by the Coulomb interaction. The exciton is an excited state, therefore relaxation to the ground state is inevitable for it. Thus, excitons have a finite lifetime. However, it is possible to relax to the ground state via some intermediate states [3].

The photoinduced absorption spectra are shown in Fig. 3. They have the same shape for the three excitation wavelengths used. The reason for this is that the photon energies of these lasers are greater than the bandgap, so the formation of excitons is preceded by the relaxation to the bottom of the conduction band.

All spectra consist of five peaks: two positive and three negative. Negative peaks correspond to an increase of the absorption, i.e. the photoinduced absorption, and the positive peaks correspond to the decrease of absorption, i.e. photobleaching of the sample. The observed spectra qualitatively correspond to the shape of the second derivative of the transmission spectrum without any excitation
(Figure 4). This shape of the photoinduced absorption would take place in the case of a broadening of the absorption lines under photoexcitation [4].

In our opinion, a simple explanation for such line broadening is associated with an inevitable presence of a nonzero electric dipole moment of excitons and the appearance of local electric fields upon photoexcitation in MoS$_2$ particles from photogenerated charge carriers – electrons and holes, as well as excitons. The position of the energy levels of excitons varies under the influence of an external electric field due to the Stark effect. For systems with a nonzero electric dipole moment, a linear Stark effect is observed. In this case, the shift of the line maximum depends linearly on $E$, i.e. depends not only on the magnitude, but also on the direction of this field relative to the axis of the dipole. As a consequence, the shift in the energy levels occurs both towards the high and low energies. Thus, different fractions of the exciton ensemble can experience shifts of different values, and this will be manifested through the broadening of the spectral components. When photoexcitation fluence increases the concentration of the local electric field sources also increases.

An open question is the long lifetime of the photogenerated charges. According to Figure 3c, the amplitude, and hence the change in the concentration of local sources of the electric field, are unchanged at laser modulation frequencies of 220 Hz and 1120 Hz, but fall by approximately 30% with an increase in the frequency to 8120 Hz. In this case, obviously, the lifetime of the charge carriers becomes comparable with the period of laser modulation. Thus, it is of the order of hundreds of microseconds. At the same time, according to the results of laser femtosecond spectroscopy, the relaxation time of the induced change in the transmission coefficient lies within the limits of units -
hundreds of picoseconds [3, 5, 6]. The magnitude of the effect in time-resolved studies reaches tens of percent, that is, orders of magnitude greater than in our observations. In our opinion, such a difference indicates that our results reflect the dynamics of the photogenerated charges localized at various kinds of defects. Time-resolved studies in turn reflect the intrinsic properties of a defect-free molybdenum disulfide.

Figure 4. Second derivative of the optical transmission spectrum of MoS₂ (red curve) and photoinduced absorption spectrum for excitation wavelength of 532 nm and modulation frequency of 220 Hz (grey curve).

Also, we note that the photoinduced absorption spectra exhibit small shifts toward higher energies relative to the second derivative of the transmission spectrum. In recent papers such shift is explained by the interactions between A and B excitons. These interactions are referred to as the "exciton self-energy renormalization". They have a repulsive character, thus the absorption peaks shift to higher energies [5].

4. Conclusion
In this paper we present the long-lived photoinduced absorption study of thin nanogranular films of molybdenum disulfide. The observed spectra consist of several positive and negative components, corresponding to an increase and decrease in absorption under photoexcitation with a laser. The qualitative agreement of the photoinduced absorption spectrum to the second derivative of the transmission spectrum in our opinion is an indication that the Stark effect is at the origin of the observed phenomenon due to interaction with the photoexcited charge carriers localized at the defects.

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