Investigation of MoS$_2$ ultrathin films formed by physical vapor deposition in vacuum

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Abstract. The article presents the optical spectroscopy results of molybdenum disulfide ultrathin films deposited on Si substrates by the methods of direct current (DCMS) and pulsed (PMS) magnetron sputtering MoS$_2$ target in vacuum, and also at flow deposition under the influence of external magnetic field on the substrate. Furthermore, the article reviews the results of optical bandgap calculation for all samples of MoS$_2$ thin films.

1. Introduction

The investigation of the two-dimensional (2D) materials is one of the budding areas of nanoelectronics for creating experimental devices with high functional properties and minimal energy consumption. In recent years researches on 2D-material such as graphene were phenomenally successful [1]. Due to its unique electronic properties, graphene attracts the interest of researchers as a 2D material for nanoelectronic's area [2]. The disadvantage of graphene is the absence of the bandgap energy in its electronic structure. This fact is an obstacle for a number of applications in the field of optoelectronics and discrete electronic. This limitation has led to the search and investigation of an alternative 2D materials that exhibit semiconductor properties. Such materials typically have a crystalline structure similar to graphite. The presence of weak “Van-der-Waals” forces between atoms located in different layers and strong bonds within the layers, allowed the researchers to separate weakly bound layers and obtain the first graphene samples. Molybdenum disulfide (MoS$_2$) belongs to the group of transition metal dichalcogenides (TMDs). Molybdenum disulfide (MoS$_2$) has a resembling graphite layered structure. MoS$_2$ is endowed with semiconducting properties and this material has been the subject of intensive research in recent years.

Molybdenum disulfide is one of the most studied farsighted materials for nanoelectronic and optoelectronic devices due to its unique electronic, mechanical, and optical properties [3]. The bulk crystal of molybdenum disulfide is a semiconductor with an indirect bandgap of 1.24 eV. With a decrease in the number of MoS$_2$ monolayers, the bandgap width increases. The bandgap width value for molybdenum disulfide monolayer reaches the value of $\approx$ 1.8 eV. An important characteristic of semiconductors is a charge carrier mobility, which determines the frequency characteristics of electronic devices [4]. The high charge carrier mobility in the molybdenum disulfide layers is according to the zero mass of the ambipolar electron-hole pairs. The maximum current carrier mobility of a MoS$_2$ monolayer reaches 500 cm$^2$·V$^{-1}$·s$^{-1}$. The transparency of the molybdenum disulfide monolayer is characterized by a high optical transmittance of $\approx$ 98.3%, which exceeds the known
value for graphene (97.7%) [6]. This set of properties determines the promising possibilities of using molybdenum disulfide with graphene as element base materials for thin transparent semiconductor systems.

The relevant objective is to develop methods that provide high-quality, homogeneous, textured MoS$_2$ ultra-thin films on large-sized substrates. Magnetron sputtering of a cathode target is one of the most future methods of applying MoS$_2$ thin films. The physical vapor deposition (PVD) method, and especially magnetron sputtering, promotes the growth of films with the desired grain size, thickness and morphology. Bulk molybdenum disulfide is a non-magnetic material. However, the molybdenum disulfide molecule is asymmetric, and each electron spin has its own magnetic moment. It is assumed that the intrinsic magnetic moment of MoS$_2$ molecules can be used to realize orientation effects during film deposition under the conditions of an applied magnetic field. The influence of an external magnetic field will orient the molecules of MoS$_2$ and integrate them, into the structure, forming the texture of the film. The aim of this work was to assess the influence of an external magnetic field, applied in the region of the silicon substrate surface during magnetron sputtering on the optical and electronic properties of ultrathin MoS$_2$ films.

To determine the optical characteristics of thin films, various methods such as Raman spectroscopy, spectroscopic ellipsometry, optical spectroscopy, and others are used. We used the method of the optical spectroscopy of thin films on the surface of a semiconductor material substrate. This method is based on measuring the reflection coefficient spectral values for the wavelength range. Optical spectroscopy is also the most common way to determine the optical bandgap.

2. Research methods

To calculate the bandgap width of MoS$_2$ thin films we used a methodology that includes four main steps.

At the first stage of this methodology we study the reflectivity of the MoS$_2$ thin film deposited on the Si-substrates. The measurement results are presented by reflection spectra. In this article, reflection spectra in the wavelength range from 380 to 1100 nm were obtained by using an Isovac Epsilon optical spectrophotometer.

The second step is the calculation of the MoS$_2$ thin film's absorption coefficients based on the obtained total reflection coefficient (R) of the substrate and thin film sample. The absorption coefficient can be calculated by using the Kubelka-Munk equation (1) [7].

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F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{K}{S} = \frac{2.303 \varepsilon C}{S}
\]

where \(K\) – is the absorption coefficient, \(S\) – scattering coefficient

At the third stage, the calculated values of the absorption coefficient are used to construct the dependence of the modified Kubelka-Munk function for semiconductors with an indirect bandgap \((F(R_\infty) \times h\theta)^{1/2}\) on the photon energy \(hv\), in the bandgap energy range from 1.3 eV to 2.7 eV. At the final, fourth stage, the optical bandgap is determined by the Tauc method. The method is based on a linear approximation of the modified semiconductor absorption coefficient dependence on the probe radiation energy near the low-frequency edge of the fundamental absorption band.

3. Experiments and results

To prepare samples with MoS$_2$ films, we used an experimental setup that ensured the methods implementation of constant (DCMS) and pulsed (PMS) magnetron deposition. The installation is equipped with balanced magnetron sputtering systems (MSS) with power sources that provide stabilization of magnetron operating modes. The diameter of the cathode target was 75 mm and a thickness of the sputtering target was 5 mm. In our experiment, the target purity was 99.9%. Fragments of semiconductor silicon wafers with a crystallographic orientation of [100], 10×10 mm$^2$ in size, were prepared as substrates. The substrates were preliminary degreased and dried. In the experiments, the following magnetron sputtering factors were varied: presence/absence of the external
magnetic field, the magnetron sputtering target mode (direct current or low-frequency pulsed), the substrate temperature and the discharge power, the other parameters remained unchanged. Magnetron sputtering was carried out in argon at a chamber pressure of $5 \times 10^{-1}$ Pa. Pulsed magnetron sputtering was carried out at a discharge power of 28 W, at a frequency of 50 kHz with a 40% pulse duty ratio. The main parameters of the magnetron deposition process are shown in Table 1. As a result of the work, 4 test samples of molybdenum disulfide films were obtained.

A magnetic field was applied parallel to the substrates surface. Ferrite magnets were located on the substrate holder by using a specific tooling. Magnets were arranged on the opposite sides of the silicon substrate. The magnetic induction magnitude of the longitudinal magnetic field in the center of the substrate was measured by using a teslameter and amounted to 0.30 T.

### Table 1. MoS$_2$ films magnetron deposition parameters.

| №  | MSS mode | Discharge power, W | Discharge current, A | Deposition time, seconds | Substrate temperature, °C | Cathode-substrate distance, mm | External magnetic field |
|----|----------|-------------------|---------------------|-------------------------|--------------------------|--------------------------------|------------------------|
| 1  | PMS      | 28                | 0.05                | 10                      | No heating               | 110                            | +                      |
| 2  | PMS      | 28                | 0.05                | 10                      | 200                      | 110                            | –                      |
| 3  | DCMS     | 22                | 0.05                | 10                      | 200                      | 110                            | +                      |
| 4  | DCMS     | 22                | 0.05                | 10                      | No heating               | 110                            | –                      |

Figure 1 shows the reflection spectra of MoS$_2$ samples obtained by magnetron deposition in pulsed mode and in direct current mode. Samples obtained under the conditions of an applied external magnetic field showed a higher reflectivity in the entire wavelength range. The reflection spectra nature of these samples is significantly different. The reflectivity of the samples obtained by pulsed magnetron sputtering is lower in comparison with samples obtained at constant current mode.

![Figure 1. Reflection spectra of MoS$_2$ thin films.](image)

The absorption spectra (Figure 2) of experimental samples were obtained by using the Kubelka-Munk function (1) that converts the reflection coefficient into absorption coefficient. MoS$_2$ film samples that were formed without external magnetic fields exhibit more pronounced absorption peaks.
4. Analysis and discussion
Based on the absorption spectra for all samples, we obtained graphs of the modified absorption function, which are shown in figure 3. In the case of applying an external magnetic field in direct current mode, the bandgap of the MoS$_2$ film increases from 1.73 eV to 1.78 eV. Similar trend is observed for the pulsed sputtering mode, the bandgap increases from 1.71 eV (sample obtained without external magnetic field) to 1.76 eV (sample obtained with external magnetic field). The modified absorption functions of the samples deposited under the influence of an external magnetic field have a pronounced absorption edge, which may indicate a higher degree of perfection and texture of the MoS$_2$ thin films.
Table 2. MoS$_2$ thin films samples parameters.

| №  | MSS mode | External magnetic field | Bandgap width, eV | Thickness, nm |
|----|----------|------------------------|-------------------|---------------|
| 1  | PMS      | +                      | 1.76              | 5.6           |
| 2  | PMS      | –                      | 1.71              | 4.2           |
| 3  | DCMS     | +                      | 1.78              | 4.1           |
| 4  | DCMS     | –                      | 1.73              | 3.5           |

5. Conclusions
As a result of our investigation, a significant effect of a longitudinal external magnetic field applied to the surface of a silicon substrate during magnetron deposition on the electronic and optical properties of ultrathin MoS$_2$ films was found. The obtained modified Kubelka-Munk absorption functions indicate the presence of a clear absorption boundary for MoS$_2$ film samples, which were deposited under the influence of an external magnetic field, which probably indicates their higher structural perfection. The same deposition time leads to a significant increase in the film thickness (by 20-30%) for cases of the presence of a longitudinal magnetic field with induction of about 0.3 T at the substrate surface during deposition, this fact indicates about the applied external magnetic field influence on the rate of growth films.

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