Spectrophotometric investigation of MoS$_2$ ultrathin films

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Abstract. The results of spectrophotometric and AFM researches of molybdenum disulfide ultrathin films, obtained on silicon substrates by magnetron deposition at various technological conditions are presented.

1. Introduction
In recent years, with the development of the methods for the thin and ultrathin films of various materials formation, increased the interest to the study of their new properties and applications in the two-dimensional embodiments [1–5]. Thus the synthesis of 2D materials and their application in electronic and optical engineering is one of the most important directions in nanoelectronics, which appeared relatively recently, this direction originated from the moment of the first publications on the study of graphene. Due to the peculiarities of the layered structure of some materials, which are characterized by the presence of weak bonds between the atomic planes, a new group including of these materials, and called the “Van der Waals materials”, appears. The most known and studied representatives of this group are disulfides and diselenides of Mo and W. Disulfides of Mo and W (MoS$_2$ and WS$_2$) are semiconductors in their properties and are of particular interest as promising 2D materials. Experimental samples of electronic and optical devices based on monomolecular layers of MoS$_2$ and WS$_2$, such as field-effect transistors [6], photodetectors [7], plasmon generators [8] and others, have high functional characteristics.

One of the most promising methods for producing thin and ultrathin films of the considering materials is magnetron deposition. Magnetron deposition parameters, such as substrate temperature, discharge power, and argon pressure, have the greatest influence on the structural, morphological, electronic, and optical properties of thin films. This work aims on estimating the influence of the working pressure and discharge power on the structural features and optical characteristics of MoS$_2$ ultrathin films deposited on various substrates.

2. Experimental part
MoS$_2$ films samples were deposited by magnetron sputtering MoS$_2$ planar target with 99.9% purity and the diameter of this target is equal to 75 mm. In accordance with the experimental plan, samples of the thin films were deposited on silicon and sapphire substrates under technological conditions, the values of which are presented in table 1. The substrates temperature was setting at 250 °C and was stabilizing by using a thermo controller and remained constant for all experiments. The target-to-substrate distance was 50 mm and the deposition time was 1 min. High-purity argon was used to sputter the target. The deposition of thin films was carried out simultaneously on both types of substrates. The surfaces of the substrates were treated with an argon ions flow at a pressure of $10^{-1}$ Pa before the deposition.
The thickness and morphological features of the prepared samples with MoS$_2$ films were measured with an atomic force microscope (AFM). The thickness was measured by stepwise profiles prepared using contact masks attached on substrates surface before the films deposition. Measured films thickness was from 12 to 96 nm. The parent surface RMS roughness for sapphire substrates was less than 1 nm, and for silicon less than 3 nm. Prepared samples were investigated by AFM Solver NEXT NT-MDT. Roughness values and average grain sizes were measured by using the AFM grain analysis software. For example, the AFM image of the surface morphology of a MoS$_2$ film with a roughness of 2.152 nm and an average grain size of 75.2 nm, obtained with the technological regimes for sample No. 4 on a silicon substrate, is shown in figure 1.

Table 1. The deposition conditions of MoS$_2$ films on substrates.

| No | Sample | Substrate temperature, °C | Discharge power, W | Argon pressure, Pa | Substrate |
|----|--------|---------------------------|-------------------|------------------|-----------|
| 1  | 2      | 250                       | 10                | 5×10$^{-1}$      | Si        |
| 2  | 2      | 250                       | 10                | 9×10$^{-1}$      | Si        |
| 3  | 2      | 250                       | 30                | 5×10$^{-1}$      | Si        |
| 4  | 4      | 250                       | 30                | 9×10$^{-1}$      | Sapphire |
| 5  | 5      | 250                       | 50                | 5×10$^{-1}$      | Sapphire |

Figure 1. AFM images for film sample No.4 on a Si substrate: 3D image of the surface on an area of 1×1 μm$^2$ (a); contrast 2D image (b); grains structure (c) and their size distribution (d).

3. Results and discussion

The spectrophotometry method was used to determine the optical characteristics of the obtained samples. The reflection spectra of MoS$_2$ films were obtained in the wavelength range from 380 to 1100 nm with in steps of 2 nm. In this work for the thin films samples bandgap determination the next methodic was applied.
The Kubelka-Munk-Gurevich equation (1) was used to convert the reflection spectra $R(\lambda)$ into a differential absorption spectrum.

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

where $K$ – is absorption coefficient, $S$ – is scattering coefficient, $R_{\infty} = \frac{R_{\text{sample}}}{R_{\text{substrate}}}$.

Based on the well-known Tauc relation (2) and using the method of graphic extrapolation of linear regions of dependences $(K\varepsilon\theta)^\frac{1}{2} \approx (h\varepsilon - E_g)$, the bandgap of MoS$_2$ films was estimated. Molybdenum disulfide with a thickness of more than one monolayer is an indirect gap semiconductor, so the coefficient equal to $\frac{1}{2}$ was used in the Tauc equation. The example of graphic extrapolation is shown in figure 2.

\[
(K\varepsilon\theta)^\frac{1}{2} \approx (h\varepsilon - E_g).
\]

where $h\varepsilon$ – is photon energy, $K$ – is absorption coefficient, $E_g$ – optical bandgap.

Generalized measurement results are presented in table 2.

**Figure 2.** Determination of bandgap by the Tauc method for a MoS$_2$ thin film on a sapphire substrate. The linear part of the graph is extrapolated to the x-axis.

**Table 2.** Results of the investigation of MoS$_2$ film samples

| No | Sample | Substrate | Discharge power, W | Argon pressure, Pa | Average grain size, nm | RMS roughness, nm | Bandgap, eV |
|----|--------|-----------|--------------------|-------------------|------------------------|------------------|-------------|
| 1  | Si     | 10        | $5 \times 10^{-1}$ | 141               |                        | 0.787            | 1.50        |
| 2  | Si     | 10        | $9 \times 10^{-1}$ | 125               |                        | 2.063            | 1.39        |
| 3  | Si     | 30        | $5 \times 10^{-1}$ | 134               |                        | 1.618            | 1.35        |
| 3  | Sapphire | 30      | $5 \times 10^{-1}$ | 70.7              |                        | 1.319            | 1.41        |
| 4  | Si     | 30        | $9 \times 10^{-1}$ | 175               |                        | 2.152            | 1.34        |
| 4  | Sapphire | 30      | $9 \times 10^{-1}$ | 36.3              |                        | 1.847            | 1.51        |
| 5  | Si     | 50        | $5 \times 10^{-1}$ | 66.3              |                        | 2.622            | 1.33        |
| 5  | Sapphire | 50      | $5 \times 10^{-1}$ | 34.3              |                        | 1.660            | 1.46        |

For MoS$_2$ thin films deposited on Si substrates with the increasing of discharge power from 10 W to 50 W, the surface roughness increases from 2.063 nm to 2.622 nm and the average grain size...
decreases from 125 nm to 66.3 nm. For MoS$_2$ thin films deposited on sapphire substrates, the increase in the working pressure leads to an increase in the surface roughness and a decrease in the average grain size twice. At higher pressures, increasing the discharge power from 30 W to 50 W slightly reduces the size of the grains on both types of substrates.

4. Conclusions
The surface roughness of MoS$_2$ films increases with the increasing of discharge power and the argon pressure. The grain size of MoS$_2$ films increases with the decreasing of discharge power and working pressure.

MoS$_2$ films on sapphire have a smoother surface, higher reflectivity and higher bandgap values in comparison with MoS$_2$ films obtained on silicon substrates. MoS$_2$ films deposited at a lower discharge power and a higher argon pressure have a lower optical reflection.

Thus, based on the data of AFM studies, it can be noted that discharge power and operating pressure decreasing leads to the planarity of MoS$_2$ thin films on silicon and sapphire substrates increasing. With discharge power decreasing at the same deposition process time, the thickness of the films decreases which leads to an increasing MoS$_2$ films bandgap.

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