Initial growth state MoS$_2$ thin film by magnetron sputtering

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Abstract. MoS$_2$ thin films were grown on sapphire substrates by the MoS$_2$ target magnetron sputtering, using the DC mode in Ar atmosphere at the substrate temperature of 200 °C for 10, 20 and 30 sec. The results of AFM studies have shown that the morphology of MoS$_2$ thin films changes significantly with the increase of the process time. At the initial stage of growth, after 10 sec of deposition, a continuous film about 3.5 nm thick was observed.

1. Introduction
Recently, molybdenum disulfide (MoS$_2$) has attracted considerable attention because of their potential for future applications in nanoelectronics, due to its outstanding electronic and optical properties of MoS$_2$ thin films. These unique properties make MoS$_2$ suitable for various applications, such as field-effect transistors with low power consumption and high-quality switching, touch and optical devices for the next generation of nano- and optoelectronics [1, 2]. In this regard, there is a problem of reproducible production of high-quality MoS$_2$ ultra-thin films using modern industrial-oriented methods. Among the deposition methods [3-5] magnetron sputtering is the most common method of forming a continuous high-quality ultra-thin films at a relatively low substrate temperature [6]. However, to use the magnetron method for MoS$_2$ ultrathin films, it is necessary to determine the relationship between the technological conditions of their formation and structural characteristics. These conditions determine the degree of homogeneity and phase composition, which, in turn, affect the morphology and electronic properties of the film. One of the main advantages of a magnetron sputtering is the ability to control the properties of the growing film and change the deposition rate by selecting operating parameters (power mode sputtering, the working pressure, the ion current density, etc.). The aim of the present work was to study the initial growth stage of MoS$_2$ ultrathin films.

2. Experimental
The experiments were carried out on technological equipment placed inside a vacuum chamber with dimensions of 46 cm in height and 40 cm in diameter. Previously, experiments were performed on the study of MoS$_2$ thin films, obtained by magnetron sputtering at low temperatures [7] and various technological parameters of the process [8]. In the present series of studies, films were deposited by sputtering a molybdenum disulfide target with a diameter of 75 mm, purity of 99.9% and high purity argon (99.9995%) was used as a plasma-forming gas. Sapphire plates about 1 cm$^2$ in size with a surface roughness of 0.877 nm were used as substrates. Before deposition, the substrate surface contamination was cleaned in an ultrasonic bath in an alkaline solution and ethanol for 10 min. The process chamber was pumped out to a residual pressure of $10^{-3}$ Pa. The main technological parameters of all MoS$_2$ deposition processes were constant, their values are given in Table 1. To estimate the
initial stage of film growth, the deposition of a flow sputtered from the target surface for 10, 20, and 30 seconds was used. The substrate temperature was controlled by a thermostat with feedback of the heater and temperature sensor and maintained at 200 °C. The distance between the target and the substrate was 10 cm. The surface morphology and film thickness were measured by using atomic force microscopy.

Table 1. Deposition process parameters applied for the samples.

| №  | Deposition time, seconds | Substrate temperature, °C | Discharge power, W | Discharge current, A | Argon pressure, Pa |
|----|--------------------------|---------------------------|-------------------|--------------------|-------------------|
| 1  | 10                       | 200                       | 22                | 0.05               | 5×10⁻¹           |
| 2  | 20                       | 200                       | 22                | 0.05               | 5×10⁻¹           |
| 3  | 30                       | 200                       | 22                | 0.05               | 5×10⁻¹           |

3. Results and discussion
The results of AFM scanning of the MoS₂ films surface deposited on a sapphire substrate during different deposition times are shown in Figure 1. Ultrathin films with a thickness of 3.5 nm were obtained for samples No.1 (Figure 1a), which were deposited for 10 sec. The surface of the film for sample No.1 had a low roughness and high planarity, the measured value of the root-mean-square roughness (RMS) was only 0.2 nm. It is known that the value of surface energy for a MoS₂ crystal along the planes of the sulfur layer (γ_f) is less than the surface energy of the sapphire substrate (γ_s), therefore, at the initial stage, a film can be formed by a two-dimensional growth mechanism. In this case, molecules arriving on the film growth surface, if they have sufficient energy, can travel considerable distances in order to adsorb to areas with high potential energy, which are the vacancies or steps of the growing film. Judging by the smooth surface and high planarity of the films obtained at the minimum time of deposition and the parameters used in the initial stage, the mechanism of layer-by-layer growth of the MoS₂ film is realized.

With an increase in deposition time of up to 20 seconds, a film is formed with a slightly larger roughness. Deposition time further increase up to 30 seconds, results in multiple increase of roughness, which can be interpreted as a change in the growth mechanism from “layer-by-layer” to “layer-plus-island”. In addition, large islands formation (Figure 2c) was observed on the sample No.3 surface. The surface morphology of MoS₂ films for samples No.2 and No.3, which were obtained for 20 and 30 sec, respectively, shown in Figure 2b and 2c, the values of surface roughness were approximately 0.25 and 0.65 nm.

Figure 1(a, b, c). MoS₂ films deposited on sapphire substrates during different process times AFM 3D images (1×1 μm²): (a) sample No.1 (10 sec); (b) sample No.2 (20 sec); (c) sample No.3 (30 sec).
With an increasing of deposition time, a proportional increase in the film thickness was observed from 3.5 nm to 7 nm, and 12 nm (Table 2). Using the software for analyzing the grain structure on the scan surface, images of grain boundaries and their distribution over the surface were obtained (Figure 2), and the values of the average grain size for film samples were determined (Table 2). With an increasing of deposition time, an enlargement of the grains and an increase in their average size was observed. Summary results of all films parameters measurement are given in table 2.

![Figure 2(a, b, c). AFM 2D images (1μm×1μm) of MoS₂ films grains structure for the experimental samples: (a) sample 1 (10 sec); (b) sample 2 (20 sec); (c) sample 3 (30 sec).](image)

From the analysis of the obtained images, it shows that, a structure is formed consisting, presumably, of planar two-dimensional grains, with observed slight differences in their surface level in height with low deposition time (10 seconds). As the deposition time increases to 20 seconds, there is a slight increase in the average grain size, which may be due to the appearance of some small number of larger island formations, probably caused by the formation of islands already on the surface of a continuous MoS₂ film. On the surface of samples obtained by deposition for 30 seconds, island formation on the surface of the film become larger and their number increases.

| Sample          | Thickness, nm | RMS, nm  | Average grain size, nm |
|-----------------|---------------|----------|------------------------|
| 1. MoS₂ Depos.10 sec. | 3.5          | 0.203    | 9.4                    |
| 2. MoS₂ Depos.20 sec. | 7.0          | 0.250    | 12.9                   |
| 3. MoS₂ Depos.30 sec. | 12.0         | 0.654    | 32.0                   |

4. Conclusions
Thus, as a result of deposition and film growth, MoS₂ films with a thickness of 3.5 nm formed on the sapphire surface during the first 10 seconds, which corresponds to approximately five molecular layers of MoS₂, characterized by low roughness and high surface planarity, the “layer-by-layer” film growth is implemented at this stage. With an increase in the deposition time, the “layer-by-layer” growth mechanism is replaced by a “layer-plus-island” growth mechanism. With a film thickness of 12 nm, which was formed in 30 seconds, on the surface of the film, relatively large island formations are observed, which significantly increase the average roughness value recorded by the AFM method.

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