MoS\textsubscript{2} ultrathin films vacuum deposition and its AFM investigation

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Abstract. In this article, we present the results of AFM studies on molybdenum disulfide ultrathin films (with a thickness of 3 to 13 nm) deposited on silicon substrates in vacuum by the magnetron sputtering MoS\textsubscript{2} target during 10, 20 and 30 seconds. The film samples structural features were estimated and the deposition time influence on surface roughness, crystals size and its distribution asymmetry, fractal dimension was determined.

1. Introduction

The publication’s number growth on the subject of 2D-materials in terms of methods and technological modes of their formation is related with an increase in the prospects interest of using 2D-materials in the field of nanoelectronics, and photonics. In recent years, the direction, connected with the production and use of films, based on molybdenum disulfide (MoS\textsubscript{2}), shows a rapid increase publication activity. This trend is characterized by a more than fourfold increase in the number of annual publications for 2017 and 2018 compared with 2013 and more than 16 times higher than this index for 2011, when the first report on the implementation of a field effect transistor based on a monomolecular MoS\textsubscript{2} layer appeared. The modern studies results of monolayer’s and ultrathin (a few nanometers thick) MoS\textsubscript{2} films electronic-optical properties indicates that this material is promising as a 2D semiconductor material with high electronic properties. In MoS\textsubscript{2} films, the effective charge-carrier mobility can reach 500–1000 cm\textsuperscript{2}V\textsuperscript{−1}c\textsuperscript{−1} [1]. Field effect transistor based on MoS\textsubscript{2} channel is endowed with high quality switching characteristics. In such transistors, the currents of open and closed states achieved ratio of 10\textsuperscript{8} and the bandgap energy can be adjusted by changing the film thickness [3] (the bandgap energy varies from 1.2 eV for bulk material to 1.8 eV in the case of a monomolecular film layer).

Among the currently known formation methods of MoS\textsubscript{2} thin films [4], two groups of methods can be distinguished according to the general implementation principle:

1. “Top-down” – methods that use the natural structural features of MoS\textsubscript{2} crystals (layered structure of a material with weak “Van der Waals” bonds between molecular planes). At the final stage of the implementation, the weakly bound molecular plane is separated from the large crystal and transferred to the substrate. In various methods of this group, physicochemical processes that provide a decrease in the forces of interplanar interaction in a crystal may be used.
2. "Bottom-up" – methods of chemical and physical film synthesis from individual atoms and molecules. It includes CVD methods based on various reactions of the molecules synthesis from precursors with the MoS$_2$ compound condensation on the substrate surface, or chemical modification methods of the surface with a pre-deposited molybdenum-based film. As well as, it includes PVD methods bottomed with physical sputtering of the MoS$_2$ target surface with ions of the inert gas and the deposition of an atomized components stream on substrate.

Each group of these methods has specific features that are reflected on the films quality. The methods of the first group are less industrially oriented, but at the same time they provide the formation of high-quality monolayer films on local sections of substrates. The methods of the second group provide a high quality technological environment, controllability and reproducibility of processes; have good scalability of the technology and the ability to obtain uniform films on large substrates.

The magnetron deposition method, which belongs to the second group of methods, is widely used in thin-film technologies. It has been technically developed, ensures high quality and controllability of the deposition processes. The horizons for the commercial use of 2D materials are related to the possibility of reproducibly producing high-quality uniform films on large-sized substrates at relatively low temperatures. It is known that, the structural features, electrical and optical properties of thin films depend on a number of factors in the processes of physical deposition in vacuum. That is why, an urgent task is to assess the capabilities of the magnetron deposition method for the formation of MoS$_2$ ultrathin films and their structural features identifying. Film growth is accompanied by structural changes, which affected on the morphology and surface roughness, depending on the temperature of the substrate, working pressure, spray power and type of substrate. The released work [5] presents the results, which include studies of the magnetron deposition modes influence on the structural features of MoS$_2$ thin films.

The aim of this work was to obtain MoS$_2$ ultrathin films by magnetron deposition at a low discharge power in a short deposition time and to experimentally study their structural features by atomic force microscopy (AFM).

2. Experimental part

In this work, we used a vacuum processing unit that provides pumping of the working chamber to a residual pressure of 10$^{-3}$ Pa. Earlier [6], experiments were carried out to refine the deposition conditions and to study how MoS$_2$ thin films obtained at various process parameters. Silicon wafers samples with a surface roughness of less than 3 nm were used as substrates. The substrates were preliminary degreased and dried. The substrates were cleaned in alkaline solutions in an ultrasonic bath. The films were deposited by magnetron sputtering of a MoS$_2$ target in direct current mode. The diameter of the cathode target was 75 mm. In our experiment, the target purity was 99.9%. Argon with 99.9995% purity was used as the working gas. The variable process parameter was the deposition time. Other parameters were constant in all experiments. The working gas pressure was 5×10$^{-1}$ Pa. The discharge power and the magnitude of the current in the magnetron circuit were 22 W and 0.05 A, correspondingly. The substrate temperature was maintained at 200 °C. The distance between the target and the substrate was 100 mm. The deposition modes of the prepared film samples are given in Table 1. To assess the films thickness, a mask was applied to the surface. After applying the film, the mask was removed and the height difference was estimated using AFM.

| No sample | Deposition time, s | 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$^{-1}$      |
The structural features of the MoS$_2$ thin films were evaluated according to surface profile parameters. Scans were prepared at the Solver NEXT AFM manufactured by NT-MDT. Previously, the samples scanning modes were worked out to obtain surface scans with the highest quality. As a result, the contact scanning mode was selected. Scanning was carried out on characteristic areas of the entire film surface that didn’t contain visible defects in areas of 0.5×0.5 μm$^2$ with a surface tapping frequency of 0.5 Hz. Statistical roughness parameters and surface structural parameters were obtained by using IA-P9 and Gwyddion software. The film-substrate step boundary was prepared by using a mask, was scanned on an AFM, and the film thickness was measured by the height difference on the step profile. The sizes of crystals (grains), the asymmetry of their distribution, and the fractal dimension were determined. An effective and convenient way to describe the film surface in more detail is fractal image analysis. It is possible to obtain results that allow a more detailed analysis and classification of the film surface morphology and the calculation of the values of its fractal dimension by using fractal analysis of AFM surface images. To determine the morphological fractal dimension, we used the method of counting cubes and the method of triangulation, based on the description of the shape of a three-dimensional surface profile using geometric constants. In order to determine the fractal dimension of the films, computer processing of micro images of the deposited MoS$_2$ films was carried out in the Gwyddion program.

3. Results and discussion

Figure 1 shows images of the silicon substrate surface (a) and the MoS$_2$ film formed during 10 s deposition time (b). MoS$_2$ film slightly follows the relief of the substrate; still, it has a smoother surface with lower roughness. So, the roughness of the substrate and the film are equal, respectively, 1.181 nm and 0.464 nm. These results and images of the surface topography of the samples indicate a noticeable smoothing of the surface after film deposition. The films thicknesses were measured in various cross sections of the “film-substrate” step-interface. The film thickness for sample No.1 equaled 3 nm, for sample No.2 the thickness was 7 nm and for sample No.3 – 13 nm.

![Figure 1. AFM images of silicon substrate (a) and MoS$_2$ film sample deposited in 10 seconds (b)](image)

Characteristic features of the samples surface areas with MoS$_2$ films are shown in Fig. 2. The main parameters of the film surface are presented in Table 2.
a) Sample No.1, MoS$_2$ on Si, 10 s.

b) Sample No.2, MoS$_2$ on Si, 20 s.

c) Sample No.3, MoS$_2$ on Si, 30 s.

Figure 2. AFM 3D images and grain distribution on 0.5×0.5 mm$^2$ surface areas for MoS$_2$ films deposited over different times: (a) sample No.1 (10 s); (b) sample No.2 (20 s) and (c) sample No.3 (30 s).

As the result of deposition for 10 seconds a continuous film with a roughness of 0.464 nm with an average grain size of 11.805 nm is formed on the surface of the sample No.1. An increase in the application time to 20 seconds (Fig. 2b) leads to an increase in the number of grains, the average grain size decreases slightly (to 11.551 nm), and the roughness and surface area increase. Film grain
coarsening is observed with a further increase in the deposition time up to 30 seconds (Fig. 2c). Also, the average grain size increases to 12.695 nm, and the roughness and actual surface area decrease.

Table 2. Results of surface parameter’s measurements of MoS$_2$ films

| Deposition time, s | Parameter          | 10       | 20       | 30       |
|-------------------|--------------------|----------|----------|----------|
|                   | Arithmetic mean roughness, Ra, nm | 0.464    | 0.521    | 0.371    |
|                   | Asymmetry coefficient, $Rsk$       | -0.393   | -0.229   | -0.170   |
|                   | Surface area, $\mu$m$^2$           | 0.257    | 0.263    | 0.256    |
|                   | Average grain size, nm             | 11.805   | 11.551   | 12.695   |

Since the asymmetry coefficient of the structure $Rsk$ differs from zero, we can talk about the uneven crystallites distribution relative to the center of the studied area. Sample No.1 is characterized by the largest asymmetry coefficient, which indicates a significant uneven distribution of crystallites.

The fractal dimension values obtained by using the cubic counting method and the triangulation method for a scanned surface with an area of 0.5×0.5 μm$^2$ are shown in Table 3. In contrast to the root-mean-square roughness, the fractal dimension of the films surface demonstrates scale invariance in the studied range of AFM image sizes. Table 3 shows us, the values of the fractal dimension calculated by different methods are differ from each other. In addition, the used methods are characterized by different accuracy in calculating the fractal dimension. It is known that the method of counting cubes has a smaller error in determining the value, in contrast to the triangulation method. Some surface smoothing irregularities occurs to the fact that during fractal analysis we use the triangulation method. Also, averaging the results entails less accuracy in the estimation of fractal dimension. Therefore, we should consider the results which were obtained by using the method of calculating cubes.

Table 3. Fractal dimension of MoS$_2$ films deposited at different times (based on the results of AFM image processing by different methods).

| Deposition time, s | Cube counting method | Triangulation method |
|-------------------|----------------------|----------------------|
| 10                | 2.406                | 2.453                |
| 20                | 2.438                | 2.482                |
| 30                | 2.443                | 2.493                |

The values of the fractal dimension obtained by using the method of counting cubes vary in a fairly narrow range from 2.406 to 2.433. The increase in fractal dimension depends on the deposition time increase. As a result, the surface morphology becomes more uniform, causing a gradation of its fractal properties. In the light of the lower roughness and actual surface area obtained for films with deposition times of 10 and 30 s, it is possible to note the presence of a higher planarity of the surfaces of these samples in comparison with sample No.2. This situation may be characteristic of the mechanism of two-dimensional growth of islands according to the type of layer-by-island growth. An increase in surface roughness was observed at the 20 s deposition stage. It may be caused with new islands grows out at planar surfaces previously formed. With further deposition (up to 30 seconds), two-dimensional growth of the islands leads to a decrease in roughness and an increase in planarity of the film surface.

4. Conclusions

The study’s results indicate a significant (more than 2.5 times) decrease in the surface roughness of silicon substrates after the MoS$_2$ films deposition. The most probable, this may be due to the
predominance of the preferential incorporation processes of MoS$_2$ molecules into the nodes formed by steps and kinks of the surface and the presence of a mechanism of two-dimensional islands growth and steps at the initial stage of film growth.

The minimum thickness of the obtained MoS$_2$ films was 3 nm and it was achieved by deposition of a particles stream sputtered from the target for 10 seconds. The thickness of the films obtained by deposition for 30 seconds was 13 nm. As a result of our work, no significant effect of the deposition time on the roughness and grain size of the films were revealed. However, with an increase in the deposition time, a steady decrease in the asymmetry coefficient and a slight increase in the fractal dimension were observed.

References
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