Formation of ultrathin MoS$_2$ films using laser-based methods

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Abstract. A comparative analysis of the abilities of several novel methods to produce ultrathin molybdenum disulphide (MoS$_2$) films containing from 1 to 10 molecular layers was carried out. To deposit MoS$_2$ films and MoO$_x$ precursor films, the atomic flux was formed by laser ablation of Mo, MoS$_2$, and MoO$_3$ targets. Saturation with sulphur of the deposited layers was performed using a reactive gas (hydrogen sulphide) or by thermally activated treatment of thin-film precursors in a sulphur vapor. It has been established that the use of hydrogen sulphide makes it possible to obtain ultrathin MoS$_2$ films at relatively low temperatures $\sim 350^\circ$C. However, these films contained local defects which were absent in the films prepared by the treatment of thin film MoO$_x$ precursors in sulphur vapours at higher temperatures ($\geq 650^\circ$C).

1. Introduction

Transition metal dichalcogenides (TMDs), such as MoS$_2$, are of particular interest to researchers, since the specific structure the TMDs allowed to form ultrathin films (2D and quasi-2D) containing the required number of mutually oriented molecular planes [1,2]. Studies of 2D-TMD materials continue to develop rapidly that is due to the discovery of new interesting electronic and optical properties. In many cases, the electronic, photonic, and mechanical properties of the 2D materials are fundamentally different from those of bulk TMD materials. Therefore, these 2D materials have great prospects for a number of new applications, including flexible electronics, spintronics, optoelectronics, catalysis etc. [3,4].

The success of the application of these materials largely depends on the success of the development of technology for obtaining them on sufficiently large areas of substrate. It is necessary to have technologies for reproducible deposition of various 2D materials with specified properties. For the preparation of heterostructures based on these thin-film materials, it is important to reconcile the temperature regimes of formation of an individual layer. At present, the most widely used method is chemical vapor deposition (CVD) which requires sufficiently high temperatures ($\sim 700^\circ$C) to produce MoS$_2$ films [5]. The steam flow of reagents is formed by heating solid precursors of sulfur and molybdenum oxide and transferring their vapors by an argon stream. Chemical interaction of vapor flux with the surface of the substrate held at appropriate temperature causes the deposition of MoS$_2$ film.

In the case of pulsed laser deposition (PLD) of MoS$_2$ films from the MoS$_2$/S target, a physical deposition of the flux of activated Mo and S atoms is realized [6,7]. The temperature regime is determined by the conditions for obtaining high-quality ultrathin films. The aim of the work was to compare the MoS$_2$ films, to produce which several variations of the PLD were used. At the same time,
physical PLD deposition of MoS$_2$ and MoO$_x$ thin film precursors was combined with temperature activated chemical synthesis of MoS$_2$ using the reactive H$_2$S gas or vapor flux which was formed by laser ablation of S target.

2. Experimental methods
To produce ultrathin MoS$_2$ films, the PLD methods using nanosecond laser pulses were developed. Pulsed laser deposition in the traditional configuration (PLD/MoS$_2$) was applied. Laser ablation of the target MoS$_2$ was carried out in vacuum or hydrogen gas at an energy density of laser irradiation near the plasma formation threshold (1.5 J/cm$^2$). In this case, a congruent transfer of the target composition to the film was possible [8]. The substrate temperature was 650°C. In the second case, the PLD of molybdenum oxide thin films was carried out. For this purpose, the targets of molybdenum and molybdenum oxide were used. Ablation of the metal target was carried out in a residual gas (reactive PLD). The metal oxide films were subjected to sulfurization at 650°C in sulfur vapors arising from the laser ablation of the solid target S in hydrogen. Also, the thin film of molybdenum oxide was reduced in hydrogen sulfide at a pressure of 10 Pa at 350°C. For these methods, the following notation were accepted: PLD/ MoO$_x$/S and PLD/MoO$_x$/H$_2$S.

The prepared films were studied by scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), micro-Raman spectroscopy (MRS).

3. Results and discussion
Figure 1 shows the characteristic result of the investigation of an ultrathin MoS$_2$ film deposited on a sapphire substrate by the PLD/MoO$_x$/S method. The prepared film uniformly covered the surface of the substrate. On the surface, the film defects characteristic of the PLD method are visible. These are submicron particles of Mo formed during laser ablation of the Mo target in O$_2$-containing residual gas.

![Figure 1. SEM image of an ultrathin MoS$_2$ film which was obtained on a sapphire substrate by sulfurization of molybdenum oxide film previously deposited by the reactive PLD method.](image)

For the films prepared by the PLD/MoS$_2$ method, XPS studies showed that a characteristic effect of the formation of the sub-stoichiometric composition of MoS$_x$ films ($x<2$) was observed. The lack of sulfur was compensated by the introduction of oxygen and the formation of Mo-O bonds (figure 2 (a)) together with the Mo-S bonds. It should be noted that the MRS studies of these films showed that the oxygen atoms did not have a significant effect on a local packing of Mo and S atoms in the MoS$_x$ films. Oxygen could be introduced already in air into the layered structure of a film containing many defects (sulfur vacancies). No characteristic peaks corresponding to Mo-O bonds were detected on the MRS spectra (results not presented).

Because of using PLD/MoS$_2$ method, the MoS$_x$ films with a layered structure were obtained, and the number of molecular layers depended on the number of laser pulses. When 100 pulses were used for target ablation, the films possessing 2 layers were obtained (figure 3(a)). This was indicated by the results of measuring the distance between the main peaks in the MRS spectra for MoS$_2$. The number of layers $n$ was determined from the empirical dependence $\Delta f=26.45 - 15.42/(1+1.44n^{0.9})$ (cm$^{-1}$),
where $\Delta f$ is the distance between the line centers corresponding to $E_{2g}^1$ and $A_{1g}$ oscillations [7]. The positions of these lines in the MRS spectrum for bulk MoS$_2$ are shown in figure 3 (a) by dashed lines. In the same figure, squares indicate lines corresponding to the sapphire substrate.

![Figure 2](a)

![Figure 2](b)

![Figure 2](c)

**Figure 2.** XPS spectra of Mo and S for ultrathin MoS$_x$ films prepared by the different laser-based methods: PLD/MoS$_2$ (a), PLD/MoO$_x$/S (b), and PLD/MoO$_x$/H$_2$S (c).

According to the XPS studies the sulfurization of the MoO$_x$ film at higher temperature using sulphur vapor and hydrogen sulphide gas proceeded quite efficiently (figure 2 (b,c)). The XPS spectra contained only lines corresponding to the chemical bonds of MoS$_2$. The use of H$_2$S could cause the
formation of an increased concentration of molybdenum vacancies, since for these films the S/Mo ratio is 2.27. In the case of using sulphur vapor, S/Mo was ~ 2.1. The number of molecular layers formed in the MoS$_2$ films depended on the thickness of the precursor MoO$_x$. Figure 3 (a) shows MRS spectra for films possessing 5–10 layers.

**Figure 3.** (a,b) MRS spectra for ultrathin MoS$_2$ films prepared by the different laser-based methods at elevated temperatures; (c,d) MRS spectra of 2D MoS$_2$ films obtained by PLD/MoO$_x$/S on sapphire and PLD/MoO$_x$/H$_2$S on NaCl substrate at moderate temperature, respectively. The inset to (c) shows the luminescence spectrum of the film. The laser wavelength for MRS studies was 632.8 nm (a,b,d) and 532 nm (c).

Precision selection of the thickness of the metal-oxide film precursor made it possible to obtain MoS$_2$ films containing 1–2 molecular layers. Figure 3 (c) shows the MRS spectrum for such a film obtained by PLD/MoO$_x$/S on the sapphire at a sulfurization temperature of 650°C. In addition to the lines from the sapphire substrate, lines at 385.3 and 405.5 cm$^{-1}$ was observed. The distance between these lines corresponds to a monolayer film. The inset to figure 3 (c) shows the luminescence spectrum which indicates the possibility of direct-gap transitions in a quite perfect lattice of prepared monolayer MoS$_2$ film.

Attempts to reduce the temperature of sulfurization of the metal oxide film using H$_2$S gas, which is known as strong reducing agent, have shown that this process may be realized at ~ 350°C. Figure 3 (d) shows the MRS spectrum for a two-layer MoS$_2$ film obtained on a NaCl substrate by the PLD/MoO$_x$/H$_2$S method at lower temperature. In addition to the typical for MoS$_2$ film $E_{2g}^{1}$ and $A_{1g}$ lines, a peak at about 460 cm$^{-1}$ appeared. One of the possible causes of this peak was a violation of the perfection of
the local structure of MoS$_2$. A line with such a shift is observed in clustered MoS$_3$ films, and it corresponds to vibrations of apical sulfur atoms bound to three Mo atoms [9]. Also, the intensity of this peak is usually large in a quite perfect MoS$_2$ when using excitation radiation in the wavelength range 600‒700 nm.

4. Conclusions.

The use of pulsed laser radiation of nanosecond duration makes it possible to realize several modes of formation of ultrathin MoS$_2$ films. Deposition of the laser-initiated flux of Mo and S atoms during ablation of the MoS$_2$ target makes it possible to obtain films with a controlled number of molecular layers, but they contain a high concentration of S vacancies. The result of sulfurization of thin film MoO$_x$ precursor prepared by PLD method depended on the temperature of the process and the nature of the reducing agent. At sufficiently high temperatures ($\geq$650°C), qualitative monolayer films can be formed using sulphur vapor and H$_2$S gas at low pressure. The use of H$_2$S gas allowed to lower the sulfurization temperature, however this caused the formation of local disturbances in the structure of MoS$_2$ films. It should be noted that the regulation of the type and concentration of defects in ultrathin TMD films is of great importance in several practical applications, in particular, in the use of these films for the catalytic activation of hydrogen evolution reaction.

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References

[1] LeRoy B J and Robinson J A 2018 APL Mater. 6 026301.
[2] Choi W, Choudhary N, Han G H, Park J, Akinwande D and Lee Y H 2017 Materials Today 20 116–30
[3] Choi K, Lee Y T and Im S 2016 Nano Today 11 626–43.
[4] Das T and Ahn J-H 2017 Flat Chem 3 43–63.
[5] Brent J R, Savjani N and O’Brien P 2017 Prog. Mater. Sci. 89 411–78.
[6] Yang Z and Hao J 2016 J. Mater. Chem. C 4 8859.
[7] Siegel G, Subbaiah Y P V, Prestgard M C and Tiwari A 2015 APL Mater. 3 056103.
[8] Fominski V Yu, Nevolin V N, Romanov R I and Smurov I 2001 J. Appl. Phys. 89 1449–57.
[9] Fominski V Yu, Romanov R I, Fominski D V and Shelyakov A V 2017 Thin Solid Films 642 58–68.