Synthesis and properties of the molybdenum and tungsten disulfide thin films

A L Zinnatullin, I R Vakhitov, A I Gumarov, S I Nikitin, S S Kharintsev, I V Yanilkin and R V Yusupov
Kazan Federal University, Kremlevskaya 18, 420008 Kazan, Russia
E-mail: almaz.zinnatullin@gmail.com

Abstract. In the paper results of thin film synthesis and primary characterization of molybdenum and tungsten disulfides are presented. The synthesis is performed by means of the high-temperature sulfurization of the metallic Mo and W films in the flow of argon. Chemical and phase compositions and morphology of thin films are reported. Optical transmission and Raman spectra are presented and discussed.

1. Introduction

Synthesis of the single-layer modification of carbon – the graphene – and studies of its extraordinary properties [1] have triggered an increased interest to two-dimensional (2D) materials. These compounds in the single layer (SL) form reveal unique properties that cannot be achieved or are even impossible in the bulk. Transition metal dichalcogenides (TMD) attract a special interest among two-dimensional materials. These compounds with the general formula MX₂, where M is a transition metal (Mo, W, Nb etc.) and X is the element of chalcogen group (S, Se, Te etc.), are layered crystals where the layers are bound to each other by Van der Waals forces. Each monolayer is in turn a “sandwich”, where the transition metal atoms are located between two chalcogen layers. Large difference between the binding energies within a layer and between the layers determines the anisotropy of TMDs.

These compounds in a single layer form are the direct bandgap semiconductors while their bulk analogues are indirect bandgap ones. These materials reveal huge potential in such fields of science and technology as spintronics, valleytronics, voltaics [2]. Therefore the development of reliable and reproducible method of TMD ultrathin film synthesis and studies of these materials are very important.

In the paper results of the synthesis and studies of MoS₂ and WS₂ thin films are presented. Films were prepared by thermal annealing in the sulfur atmosphere of the molybdenum or tungsten thin films pre-deposited by either the magnetron sputtering or molecular beam epitaxy (MBE). Chemical and phase compositions were studied by X-ray photoelectron (XPS) and Raman spectroscopies, surface morphology was investigated with scanning electron microscopy (SEM). Optical transmission spectra of ultrathin films of MoS₂ were also studied.

2. Experimental details

Initial metallic Mo and W films with the thicknesses of 3.5 nm and 10.8 nm, respectively, were obtained by magnetron sputtering onto the silicon (Si) substrates at room temperature with the sputtering power of 120 W. Molybdenum films with the thickness of 1, 2 and 4 nm on the fused silica (SiO₂) substrates and 5.7 nm film on the R-cut sapphire have been obtained with MBE. Pre-deposited...
metallic films were annealed then in an atmosphere of sulfur at a temperature of 800°C. A weak flow of ultrapure argon (~15 sccm) was used to transport gas for sublimated sulfur. After the annealing samples were cooled down to room temperature also in the flow of Ar (figure 1).

Figure 1. Disulfide film synthesis sequence (a); diagram of a setup for sulfurization of Mo and W thin films (b). Upper graph in (b) illustrates approximately the dependence of the furnace temperature on time.

3. Results and discussion
XPS measurements were performed in the ultrahigh vacuum chamber (base pressure ~ 3×10⁻¹⁰ mbar) equipped with the Mg Kα X-ray source operated at 12.5 kV and 250 W, and a Phoibos 150 hemispherical energy analyzer (all from SPECS).

Figure 2. XPS spectra of the MoS₂ and WS₂ thin films on the fused silica substrates in the energy ranges for: (a) molybdenum in 3d lines (solid line – before and dashed line – after sulfurization); (b) – sulfur in MoS₂; (c) – tungsten 4d lines.

XPS measurements (figure 2) show that the initially metallic films of molybdenum and tungsten have been successfully transformed into the disulfides of these elements during sulfurization [3]. This
is confirmed first of all by the energy shift of molybdenum and tungsten lines towards the higher binding energy range, as well as the appearance of sulfur line in the spectra. The change in energies of the Mo and W lines is the chemical shift that is associated with the displacement of the electron density in the sulfur direction during the formation of a compound. Positive charge on a metal atom creates additional Coulomb attraction of the photoelectron emitted due to the interaction with X-rays [4].

Raman spectra of molybdenum and tungsten disulfides were studied with the NTEGRA SPECTRA setup (NT-MDT). Laser emitting at a wavelength of 532 nm was used for excitation of phonons in the samples. The measurements were performed at room temperature. Matching of well-known vibrational modes [5, 6] with the peaks in experimental spectra indicates that indeed as a result of sulfurization molybdenum and tungsten disulfide films have been obtained (figure 3). Furthermore, it is well-known that phonon frequency splitting between the \( A_{1g} \) and \( E_{2g} \) modes depends on the number of layers for MoS\(_2\) [7]. Splitting of these lines in our experimental spectra is \( \sim 25 \) cm\(^{-1}\), which corresponds to 6-8 molecular layers. Rich Raman spectrum for WS\(_2\) is due to the known fact that under excitation with the 532 nm wavelength laser light, not only the first order Raman modes but also longitudinal acoustic modes of the second order are excited. In addition, there are several peaks associated with multphonon processes [6].

![Raman spectra](image)

**Figure 3.** Raman spectra of thin films for: (a) MoS\(_2\) and (b) WS\(_2\). Raman modes corresponding to the peaks are marked in spectra.

Morphology of the surface was studied with the universal scanning electron microscope Merlin (Carl Zeiss). SEM results (figure 4a) show that the investigated samples represent the nanogranular films, wherein each granule is a platelet with the thickness of several nanometers in-plane dimensions of about a hundred of nanometers. Granules have different orientations with respect to the substrate, as it also can be seen from figure 4a. Moreover, the granules have different shapes: triangular, truncated triangular, and near-round ones. Different shapes of these granules are related in the published data to the varying conditions inside the oven during the growth [8]. In particular, the sulfur concentration may vary.

Optical transmission spectra of molybdenum disulfide samples were studied using dual beam spectrophotometer SPECORD M40 (Carl Zeiss). In the spectra (figure 4b) two absorption peaks are revealed for MoS\(_2\) both on the sapphire and fused silica substrates. These peaks are associated with the excitonic states and are labelled traditionally as A and B [9]. Figure 4b shows that the position of these peaks depends on the film thickness. Namely, excitonic absorption bands shift to the higher energies on decreasing of the film thickness. Such a change in transmission spectrum is related to the band structure modification of semiconducting molybdenum disulfide with the decrease of the molecular layer number [10]. The peak position dependence on the material and structure of substrate remains poorly studied.
Figure 4. (a) SEM image of MoS$_2$ on a single crystal Si substrate; (b) optical transmission spectra of MoS$_2$ on the fused silica and sapphire substrates.

4. Conclusions
The paper presents the results of the synthesis and investigations of thin and ultrathin molybdenum disulfide and tungsten disulfide films. It was shown that applied synthesis method leads to the formation of multilayered TMD in the form of nanogranular thin films. The transmission spectra of the samples contain two excitonic absorption bands. These bands are shifted to higher energies by decreasing film thickness.

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