Investigation of the properties of two-dimensional molybdenum disulfide films synthesized by the CVD method

S Smagulova, A Semenova, E Zakharkina and P Vinokurov

Graphene Nanotechnology Laboratory, North-Eastern Federal University, 58 Belinsky Street, 677027 Yakutsk Russian Federation

E-mail: smagulova@mail.ru

Abstract. Molybdenum disulfide films were synthesized through chemical vapor deposition. Optimal synthesis parameters (temperature, time, gas pressure, gas flow rates, and geometrical arrangement of substrates and crucibles with precursors), allowing for the growth of single-layer domains of molybdenum disulfide with maximum domain sizes (250 μm), were found. The technology for processing substrates, including mechanical, chemical and plasma-chemical processing, was developed. The results of studies on the structural, optical, electrical properties of the synthesized and transferred films using optical, scanning electron and atomic force microscopes, elemental analysis, measurement of Raman scattering spectra, luminescent and electrical characteristics are presented.

1. Introduction

After the discovery of graphene and its unique properties [1], the investigation of new two-dimensional materials became one of the most popular research topics. Among such materials, the class of transition metal dichalcogenides, in particular, molybdenum disulfide (MoS2), has gained much research attention. As the other transition metal dichalcogenide family, MoS2 is widely used in many areas, such as a hydrosulfurization catalyst, photocatalyst, photocell, and as a dry lubricant, due to its distinctive electronic, optical, and catalytic properties. Multi-layer MoS2 is a semiconductor with an indirect 1.2 eV band gap [2]. However, most interesting properties appear in single-layer molybdenum disulfide, which is a direct-gap semiconductor with a 1.8 eV band gap [3]. Investigating two-dimensional MoS2 opens new opportunities in the development of new nano- and opto-electronic devices.

A number of methods for obtaining two-dimensional materials have been developed: mechanical splitting, electrochemical intercalation with lithium ions, magnetron sputtering, pulsed laser sputtering, etc [4]. The existing techniques for producing MoS2 do not allow controlling the number of atomic layers and lateral sizes of domains. Nowadays, the most promising and relatively inexpensive method for synthesizing two-dimensional MoS2 films of high quality is chemical vapor deposition (CVD) [5-7]. This method makes possible to obtain homogeneous two-dimensional MoS2 films with lateral domain sizes of up to 100 μm. The advantage of this technique is the high quality of samples grown and the possibility of material synthesis in large quantities. Raman spectroscopy is one of the main methods for characterizing two-dimensional structures that allows to obtain information on the number of atomic layers and the quality of the MoS2 structure.

MoS2 films synthesized by the CVD method can be used as active components for nanoelectronic devices or building blocks for complex layered heterostructures. Vertical heterostructures are currently
considered as the main direction of thin-film electronics development. For such heterostructures, a special name has been introduced – van der Waals heterostructures, since they are expected to be formed by sequential growth of layers, and in a single structure, the layers will be held by van der Waals forces. Currently, several types of these heterostructures, in particular, the ones based on transition metal dichalcogenides (MoS₂, WS₂) and graphene, have been developed and studied. An important achievement of the van der Waals heterostructures based on two-dimensional materials is the demonstration of the possibilities of new physical approaches and new principles for constructing electronic structures. The formation of such structures opens up many opportunities for developing various kinds of electronic devices, ranging from transistor structures and optoelectronic elements, to various gas sensors and biological sensors.

Considering the aforementioned, in this work, the effect of temperature, gas feed rate, synthesis time and location of substrates on the kinetics of formation of two-dimensional MoS₂ was studied.

2. Experimental part
Silicon with a 285 nm thick SiO₂ oxide film was used as substrate. Before the process, the substrate surface was pretreated in an ultrasonic bath with acetone and isopropyl alcohol for 5 min to remove contaminants. To remove organic bonds from the surface, the substrate was treated in a sulfur-peroxide solution in a 1:3 ratio, followed by washing in deionized water. Then, the substrate was processed in an oxygen plasma for 5 min at a power of 150 W. MoS₂ was synthesized by the CVD method in a RS 80/750/ three-zone tube furnace (Nabertherm, Lilienthal, Germany), shown schematically in figure 1.

Figure 1. Schematic illustration of a setup for CVD growth of MoS₂.

MoO₃ and sulfur powders (Sigma Aldrich, St. Louis, USA) in a weight ratio of 1:13 were used as initial precursors for the synthesis. The substrates, on which MoS₂ was grown, were located above the crucible with the MoO₃ powder. To control the synthesis, the following parameters were selected: temperature, time, pressure, argon feed rate, and precursor concentration. The whole process can be divided into five stages [8], as shown in figure 2:

1. The reaction chamber is pumped out to a pressure of 10⁻⁵ bar for 1 h.
2. When the temperature reaches 300 °C, inert gas (Ar) is fed into the chamber at a flow rate of 100 cm³/min for 1 h to a pressure of 1 atm.
3. The chamber is heated to a synthesis temperature of 700 °C.
4. The growth of MoS₂ on SiO₂ occurs in the Ar flow at a rate of 10 cm³/min for 30 min at 700 °C.
5. After synthesis, the chamber was naturally cooled to room temperature in the Ar stream at a flow rate of 300 cm³/min.
The obtained films were studied by Raman spectroscopy using an INTEGRA SPECTRA system (NT-MDT, Zelenograd, Russia) equipped with a green laser at $\lambda = 532$ nm. The morphology of the surface of the MoS$_2$ films grown by the CVD over the SiO$_2$ substrate was studied by an AFM/STM "SolverNext" scanning probe microscope (NT-MDT). The morphology and elemental composition of the films were determined by scanning electron microscopy using a JSM-7800F instrument (JEOL, Tokyo Japan). Optical images were taken by an Eclipse LV100 optical microscope (Nikon, Tokyo Japan).

3. Results and discussion

It is known that in the Raman spectra of MoS$_2$, two most intense peaks related to the vibration modes in the plane and outside the plane in the region of 400 cm$^{-1}$ can be observed [9]. The vibration modes of atoms of both molybdenum and sulfur are limited in the horizontal plane; therefore, the vibrations of atoms will be located along the vertical plane. With an increase in the number of layers, a decrease in the frequency of vertical vibrations mode will be observed, because with an increase in the number of layers, the van der Waals forces will also increase, which will suppress atomic vibrations along the vertical plane. In [9], it is shown that in the domains of the MOS$_2$ grown by the CVD method on the SiO$_2$, a decrease in the Raman peak can be observed with a decrease in the film thickness (the number of atomic layers). The frequency difference between these modes for the single-layered MoS$_2$ was found to be $\Delta \nu = 19$ cm$^{-1}$, for the double-layered MoS$_2$ - $\Delta \nu = 21$ cm$^{-1}$, and for the multi-layered MOS$_2$ - $\Delta \nu = 25$ cm$^{-1}$. Figure 3 presents the Raman spectra of the studied samples.

The analysis of the Raman spectra showed that the samples represent films of the single-layered MoS$_2$. In addition, measurements of the Raman spectra of the double- and multi-layered MoS$_2$ were carried out (figure 3).

The optical measurements showed the growth of the MoS$_2$ domains on the SiO$_2$ surface in the form of triangles (figure 4) with lateral sizes of up to 80 $\mu$m. The domain size varied depending on the location of the substrate relative to the molybdenum-containing precursor. In the samples that were located 5-7 cm from the precursor MoO$_3$, the domain size was 10-20 $\mu$m. With decreasing the distance between the samples and the precursor, the domain size increased up to 40 $\mu$m. It was experimentally established that the maximum domain size is obtained directly above the crucible with the MoO$_3$. It is possible that larger flakes were grown near the Mo precursor due the higher MoO$_3$ concentration and different gas flow through the substrate surfaces.
Figure 3. Raman spectra of the synthesized MoS$_2$.

Figure 4. Optical images of the domains grown at different distances from the MoO$_3$ precursor: more than 5 cm (a), more than 2 cm (b), and directly above the precursor (c).

The AFM measurements showed that the thickness of a single MoS$_2$ layer is 0.9 nm (figure 5). Besides, at the center and the edges of some domains, defects in the form of overgrown fragments of the same material were found.

Figure 5. An AFM image of the single-layer MoS$_2$ domains on the SiO$_2$ surface.
The data on the energy dispersive X-ray spectral microanalysis (figure 6), presented in table 1, made it possible to determine the elemental composition of the samples - molybdenum (0.19 at.%), sulfur (0.48 at.%), silicon (28.41 at.%), and oxygen (70.91 at.%). It should be noted that the spectral peaks of molybdenum and sulfur are located at the values of about 2.3 keV and have only minor deviations with respect to each other, which made it difficult to identify these elements (figure 6). Nevertheless, it was found that the atomic sulfur content is twice the atomic molybdenum content.

![Figure 6. The line-scan EDX spectrum of a selected region from the STEM image (marked by a pink color rectangle).](image)

4. Conclusion
A method for the synthesis of two-dimensional MoS₂ films by the CVD was developed. The AFM and optical measurements showed the growth of the MoS₂ domains on the SiO₂ surface in the form of triangles with lateral sizes of up to 80 μm. The domain size varied depending on the location of the substrates relative to the molybdenum-containing precursor. It was experimentally established that the maximum domain size is achieved directly above the crucible with the MoO₃. The analysis of the Raman spectra demonstrated that the grown films mostly consist of MoS₂ monolayers. Besides, the Raman spectra of the double- and multi-layered MoS₂ were measured. A decrease in the peaks of the Raman spectra peaks was observed with a decrease in the thickness of the MoS₂ film grown through the CVD method over the SiO₂ surface. The frequency difference between these modes was found to be Δν = 19, 21 and 25 cm⁻¹ for the single-, double- and multi-layered MoS₂, respectively.

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