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Formation of nanostructured films based on MoS_2, WS_2, MoO_2 and their heterostructures

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In this work thin film coatings based on WS_2, MoS_2, MoO_2 and their composites were synthesized, morphological and structural properties of deposited coatings were studied. Chemical vapor deposition with heated MoO_3, WO_3, S powder as precursors was used. Dependence of structural and morphological properties, chemical composition of deposited films on parameters of synthesis was defined. Films of vertically aligned 10 nm thick plate crystals consisting both of pure MoO_2 and MoO_2 covered with thin MoS_2 layer were obtained. Formation of polycrystalline films of regular triangular shaped WS_2 and uniform continuous 20 nm thick WS_2 films with covering area of 2×2 mm has also been observed. In this work we also report about synthesis of films consisting of regular triangular shaped WS_2 crystals and MoS_2 irregularly shaped crystals overlapping each other.

Keywords: 2D materials, transition metal dichalcogenides, heterostructures, CVD, AFM.

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Introduction

Two-dimensional materials have some unique properties, making them attractive for use in electronic devices [1], optoelectronic devices (operating in visible, infrared and terahertz wavelength ranges) [2,3] etc. The special interest to the two-dimensional materials was gained due to development of implementable manufacturing methods and active studies of two-dimensional graphene [4]. Two-dimensional materials also include hexagonal boron nitride, two-dimensional black phosphorus and the whole class of compositions known as transition metal dichalcogenides (TMD). The general chemical composition of TMD can be written as MX_2, where M is transition metal (Mo, W, etc.), and X is chalcogen (S, Se, Te). Various combinations of these elements result in forming of materials of similar crystal structure, but with different electronic properties. TMD materials include both conductors, insulators and semiconductors with various energy bandgaps and charge carrier mobility [5]. Range of possible application of TMD materials is very wide. Presence of direct area in TMD monolayers (for instance, MoS_2, WS_2) allows to create transistors and effective optical and IR emitters and detectors [6]. Strong spin-orbit interaction due to participation of *d*-electrons in creation of chemical bonds results in areas spin splitting and makes TMD materials prospective for application in spintronics [7].

Heterostructures based on two-dimensional materials with various electronic characteristics are of significant interest. Such heterostructures of two-dimensional materials can be divided into van der Waals and in-plane. Van der Waals heterostructures are two-dimensional materials layers superimposed and held together by van der Waals forces jcite8. The advantage of such heterostructures is a relatively large area of two materials contact and simplicity of their forming. Such heterostructures are usually made using mechanical detaching of two-dimensional materials layers from their volume phase and detached layers overlapping using appropriate substrates. The main disadvantage of this method of heterostructures forming is impossibility of manufacturing scaling of electronic devices based on them with good reproducibility. In-plane heterostructures are created of two-dimensional materials, chemical composition of which varies along the layer. The advantage of such heterostructures is a possibility of finer adjustment of electronic properties and heterojunction parameters due to bigger overlapping of electron clouds of two materials with different composition, as well as due to influence

of morphological characteristics [9]. Disadvantages include smaller heterojunction area and processing complexity of such heterostructures synthesis.

In literature such combinations of $2D$ materials are sometimes called $2D/2D$ heterostructures. $2D/3D$ heterostructures formed at two- and three-dimensional materials bonding are also of certain interest. Such heterostructures are also used in electronics and optoelectronics [10]. Among $2D/3D$ heterostructures the ones with metal as three-dimensional material are singled out. Depending on mutual arrangement of Fermi levels of two-dimensional material and metal, part of electrons transitions from one material to another, while forming the surface charge and Schottky barrier. Presence of surface charge significantly influences the contacts properties in semiconductor devices due to change of mutual arrangement of Fermi level of metal electrodes in relation to electrons level in semiconductor. Besides using such structures with Schottky barrier and surface charges in electronics and photonics, they are used in photochemistry and catalysis. Excess charge at two-dimensional material increases its chemical activity. When using semiconductor two-dimensional material during light absorption the additional excited electronic states, increasing material catalytic capacities, are created [11].

This, for instance, MoO_2 exhibits metallic conductivity [12], while combination of MoS_2/MoO_2 is the structure with Schottky barrier (and surface charge) and can be used both for creation of electronic devices and tasks of photocatalytic water electrolysis, for instance, for hydrogen energetics [13]. MoS_2/WS_2 heterostructures, in their turn, are of special interest for application in electronics and optoelectronics [14].

The important problem for any applications is a possibility of scaling the process of synthesis of heterostructures based on two-dimensional materials. One of the common and commercially attractive methods of two-dimensional materials synthesis is a method of chemical vapor deposition (CVD). Recent studies have shown the principal possibility for this method use for synthesis of both $2D/2D$ and $2D/3D$ heterostructures [15,16]. Conventionally used CVD chamber is a heated quartz tube with precursors and substrate inside [17]. In such configuration the control of evaporation rate and temperature of each of the precursors and substrate is highly complicated, since many parameters of CVD process remain unknown. This results in complications in observing and understanding of the forming mechanisms of $2D$ materials and heterostructures based on them in CVD processes.

In this study the results of studying the processes of forming the films, consisted of MoS_2/MoO_2, WS_2 heterostructures and MoS_2/WS_2 heterostructures on $Si(111)$ surface at chemical vapor deposition, their morphological and structural properties are presented. The feature of this study is a use of a new type of CVD method, allowing to improve accuracy of precursors evaporation rate control and to use a nonuniform heating of a substrate for implementation of the wide temperature range on it during single CVD process.

1. Experimental conditions and materials

For materials obtaining the setup, scheme of which is presented in Fig. 1, was used. The setup consists of vacuum chamber, inside of which the modified atomic force microscope (AFM) SMM-2000 (made by JCS „Zavod-PROTON“), system of sample fixation and heating, system of precursor powders heating and their vapors delivery to sample surface are located. In contrast with conventionally used CVD setups the design of the developed system includes independent heating of the precursor crucibles and the substrate. Low thermal capacity of substrate and crucibles content combined with high heating capacity provide fast temperature change up to 200°C/s and 100°C/min for the substrate and the crucibles, respectively. Another feature of this setup is the system of sample fixing and heating, providing the possibility to make AFM measurements of surface morphology of the same area on sample surface with dimensions of $20 \times 20\,\mu$m between synthesis stages with high spatial resolution and without necessity of the sample removal from a reaction chamber. This AFM system design was described in detail in our earlier work [18]. Powders of pure sulfur S, molybdenum oxide (VI) MoO_3, tungsten oxide (VI) WO_3 were used as precursors. Precursor powders were put into quartz crucibles, that may be heated to temperature of about 900°C by electrical current passage through nichrome wire wound around the crucibles. Chromel-alumel thermocouple is brought inside each crucible for the content temperature control. Quartz crucibles are tightly connected to the quartz tube, through which the inert gas-carrier argon is pumped, which flow is controlled by a needle valve. At heating the crucibles content, precursors partially vaporize, their vapors are taken by gas-carrier argon and delivered to a silicon substrate heated to temperature of about 700–1000°C. Near substrate surface the precursor molecules are thermally activated, chemically reacting with each other and, depending on the selected synthesis parameters, form a film of various chemical composition and morphology.

Precursors concentration in gaseous phase is controlled by changing the temperature of solid (or liquid) phase inside the crucible. Increase of crucible content temperature results in increase of saturated vapor pressure and, as a result, in increase of precursor molecules concentration in gaseous phase. In the performed processes of MoS_2, WS_2, MoO_2 films synthesis the temperature of S in crucible varied from 110 to 200°C, while temperature of MoO_3 and WO_3 — from 600 to 900°C. At such precursor temperatures S comes into gaseous environment mainly as S_8 molecules, however vapors composition includes various number of molecules, containing lesser number of atoms, including single atoms of sulfur [19]. MoO_3 and WO_3 at such temperatures are

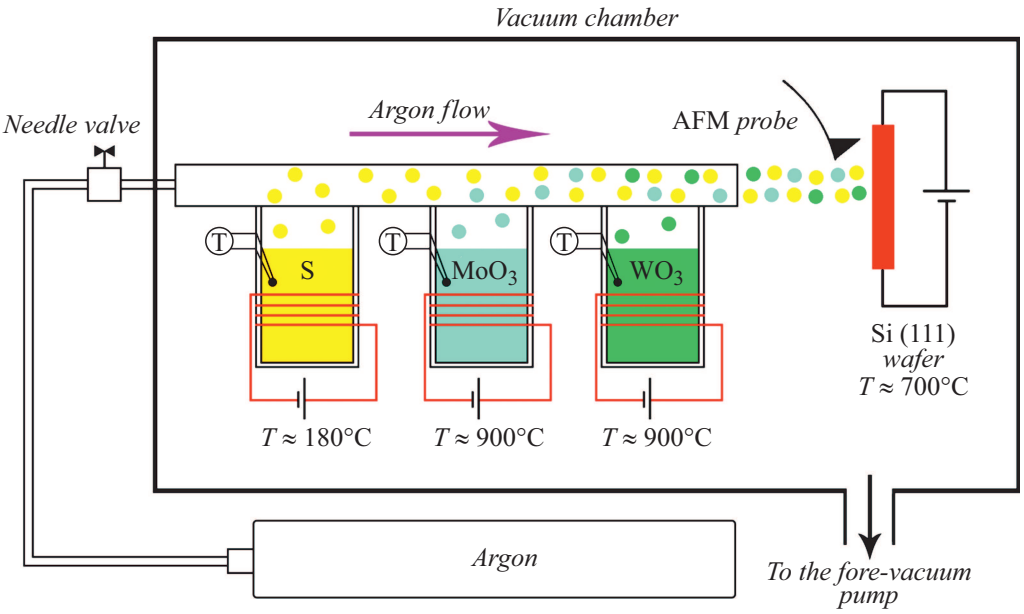

Figure 1. Scheme of setup in use.

sublimated and come into gaseous environment mainly as the molecules of MoO_3 and WO_3.

Single-crystal silicon plate with orientation of (111), thickness of 0.6 mm and area of about 14×7 mm, was used as a substrate. Due to specifics of the plate cutting procedure, its shape was not perfectly rectangular, but this circumstance is not important for the further studies. Silicon substrate heating was performed by electrical current passage through it. Electric voltage is supplied to the substrate using electrodes made of molybdenum wire in such way that the resulting contact of electrode with the silicon sample is almost point-contact. Such configuration allows to provide non-uniform heating of the substrate, on surface of which the stationary temperature distribution is established. Control of temperature distribution over the substrate surface is performed as per emission color, that was registered by photographing the heated sample. Dependence of thermal emission color of the silicon substrate on a photographic image from temperature was pre-established using the reference pyrometer Cyclops 100. Obtained photographic images were analyzed using specially developed software means, allowing to make a map of temperature distribution on the substrate surface. Example of photographic image conversion into a temperature distribution map is presented in Fig. 2. Non-uniformity of sample heating was used for research of structural-morphological properties and chemical composition dependence on substrate temperature by means of measuring the corresponding parameters in various points on the sample surface.

In this study in all CVD experiments the chamber was pre-pumped to pressure of $1 \cdot 10^{-2}$ mbar, argon flow was set in such a way for the pressure in the chamber to be $8 \cdot 10^{-1}$ mbar, settling time in all experiments was 10 min.

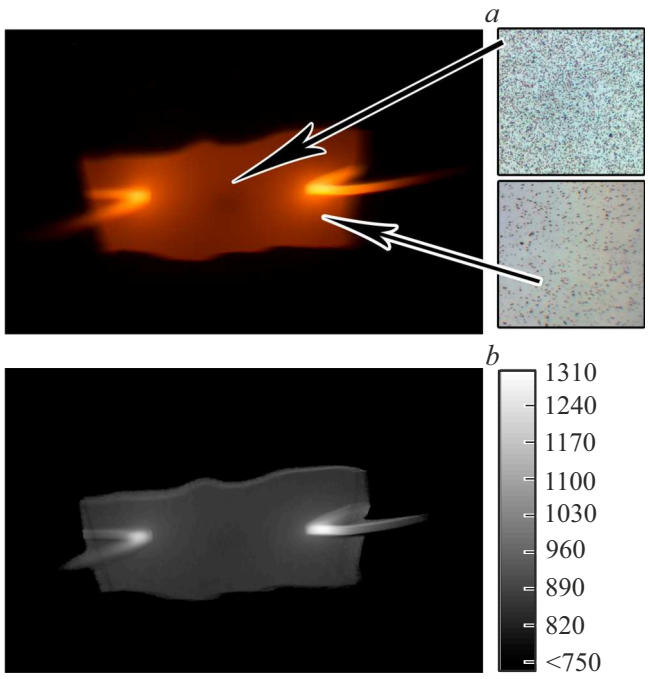

Figure 2. *a* — picture of original heated sample; *b* — calculated temperature distribution map, setups are in °C. Optical micrographs in the upper right corner show the difference of crystallites settling density on the substrate in various points on its surface. Optical micrographs dimensions are $20 \times 20\,\mu$m.

Structural-morphological properties of observed materials were studied using scanning electronic microscope (SEM, Supra 40, Carl Zeiss), micro-Raman spectrometer (HORIBA LabRAM HR Evolution UV-VIS-NIR-Open at excitation by laser radiation of Nd:YAG 532 nm, 14 mW)

and modified atomic force microscope SMM-2000 (JCS „Zavod-PROTON“).

2. Results and discussion

For the purpose of observing the CVD synthesis conditions, providing formation of film materials with the required characteristics, the series of sample processes with various parameters were performed. During these experiments it was observed, in particular, that at the temperature of S below 180°C, substrate temperature below 900°C and temperature of MoO_3 equal to 800–900°C, a film coating, visible through optical microscope, is formed on the substrate. The study using SEM showed (Fig. 3, *a*), that samples, observed at these conditions, present an array of vertically aligned plate crystallites with thickness of about 10–20 nm. Besides, it was observed that the crystallites arrangement density on the surface depended on local substrate temperature and varied from 2 pieces per μm^2 at temperature of the substrate of 700°C to 0.3 pieces per μm^2 at temperature of 850°C. At the substrate temperature above 900°C there were no crystallites on the substrate observed. Performed Raman spectrometry study demonstrates that the observed crystallites are crystals of monoclinic MoO_2. Fig. 3, *c* shows the characteristic Raman spectrum observed for samples with such crystals. Series of peaks

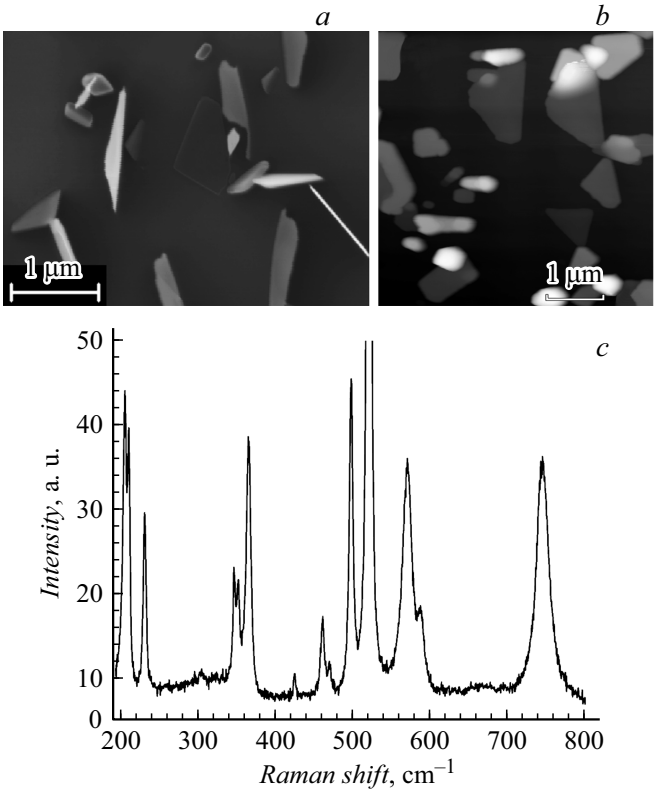

Figure 3. Characteristic (*a*) — SEM image of plate crystallites of MoO_2; *b* — AFM image of crystallites; *c* — Raman spectrum of deposited film, all lines except located at 520 cm^{-1} (silicon line) correspond to the structure of monoclinic MoO_2.

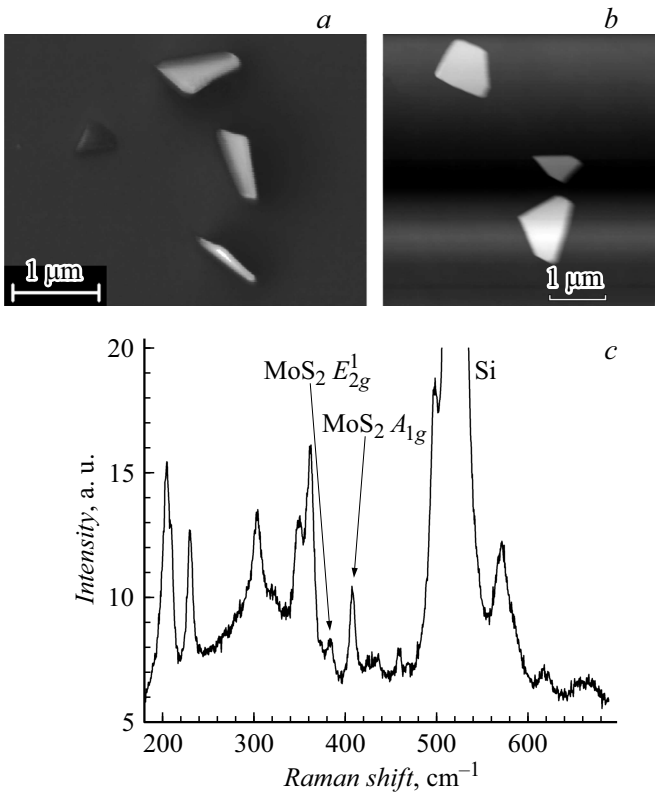

Figure 4. *a* — SEM image of crystallites of MoS_2/MoO_2; *b* — AFM image of crystallites; *c* — Raman spectrum of MoS_2/MoO_2; arrows show the characteristic lines of MoS_2.

at 204, 230, 350, 364, 496, 568, 741, 817 cm^{-1} definitely confirms crystal structure of monoclinic MoO_2 [20]. The line at 520 cm^{-1} is a Raman spectrometry signal from the silicon substrate. Typical AFM image of MoO_2 crystallites is presented in Fig. 3, *b*. It should be noted that during scanning the AFM probe pulls plate crystallites away from the substrate and arranges them in horizontal plane. This becomes obvious, when comparing the corresponding AFM and SEM images, and also considering the fact that at the first scanning the AFM image has specific noises in the form of irregular emissions, but at the second scanning of the same area these noises disappear. AFM measurements allowed to confirm the thickness (established earlier using SEM) of plate crystallites, characteristic size of which was 10–20 nm.

At temperatures of S heating above 180°C, substrate temperature below 900°C and temperature of MoO_3 heating of 800–900°C the similar film is formed as an array of vertically aligned plate crystallites. Despite the lack of specific differences in optical, electronic and AFM images between these crystallites and the ones described earlier (Fig. 3, 4), their Raman spectra includes lines at 383 and 407 cm^{-1}, indicating the formation of a layer (more than 4 monolayers) of two-dimensional material of MoS_2 on a surface of plate crystallites of MoO_2. Such materials are further designated as MoS_2/MoO_2. Also, in

Raman spectra of these MoS_2/MoO_2 crystallites the line appears at 303 cm^{-1}, supposedly related to sulfurization of the silicon substrate during CVD synthesis process [21]. Growth of similar vertically aligned plate crystallites was observed, for instance, by authors of [22] with significant difference in methods of settling, substrate types and chemical composition of a layer on a surface of MoO_2 crystallites in contrast with the ones, used in this study.

To observe the parameters of CVD synthesis of the created setup, providing WS_2 formation, the series of experiments was performed, when crucible with powdery WO_3 was heated to temperature of about 800–900°C, while crucible with sulfur — to temperature of 120–140°C. At substrate temperature of 950°C the film, visible through optical microscope, is formed on the substrate. The study using SEM showed (Fig. 5, *a, b*), that the resulting samples are combination of crystallites of regular triangular shape with various thickness, thus implying on successful settlement of WS_2 crystallites. The performed Raman spectrometry study confirmed the assumption that the resulting crystallites are crystals of hexagonal WS_2. Raman spectra (Fig. 5, *c*) clearly show the characteristic lines of WS_2 at 354 and 418 cm^{-1}. Based on general shape and positions of these lines it can be concluded that crystallites with more than four layers dominate in the deposited film [23]. Besides SEM studies revealed the nanometric size particles on crystallites surface. Crystallites of regular triangular shape with significantly smaller lateral sizes and thickness were also observed. Presence of two types of crystallites, significantly different in thickness, as well as nanometric particles on the surface of these crystallites can indicate the two-stage growth mechanism. As per this mechanism, initially with a small rate (due to mismatch of parameters of Si crystal grating and deposited material) the crystallites of WS_2 with thickness of several atomic layers and lateral size of up to 200 nm are formed, and then on their surface and with higher rate (due to match of crystal gratings) the nanometric size particles are settled, and while combining they create new layers and increase crystallites thickness.

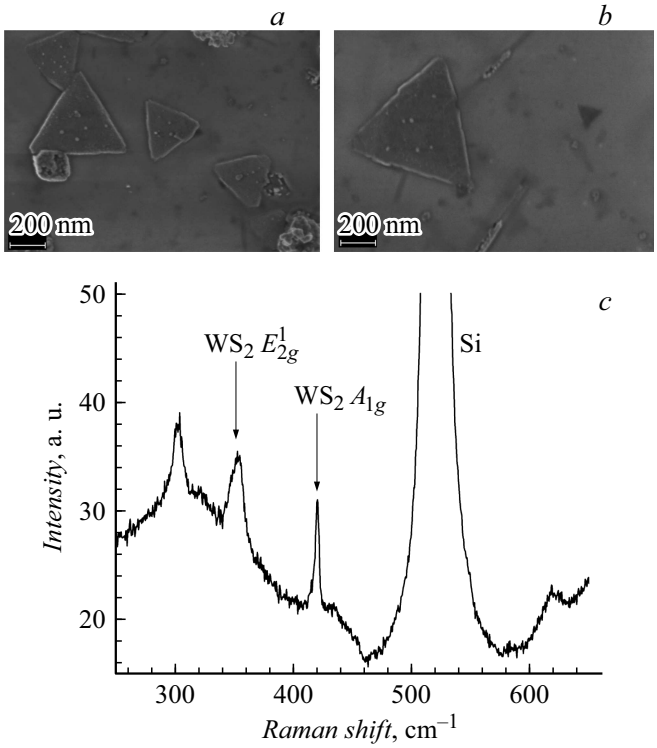

Figure 5. *a, b* — SEM images of crystallites of WS_2; *c* — Raman spectrum of the film, containing crystallites of WS_2 of triangular shape.

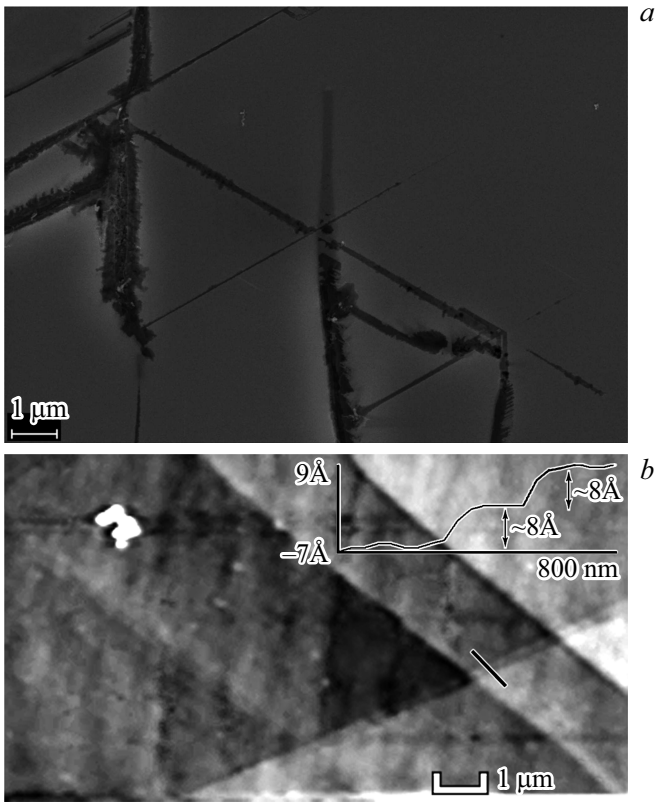

Figure 6. *a* — SEM image of homogeneous film of WS_2 with visible ruptures; *b* — AFM image away from ruptures. Profile of steps with characteristic sizes is presented in the corner.

The further increase of substrate temperature results in formation of more homogeneous coating and, for instance, near 1100°C the film of WS_2 becomes continuous and can cover large areas on silicon substrate. Typical SEM image of such film is presented in Fig. 6, *a*. There are dark bands, that are film ruptures, formed during the sample cooling due to differences in thermal-expansion coefficients of the film and underlying silicon substrate. Characteristic rupture depth, defined using AFM measurements, was 5–20 nm, that can be taken as the thickness of WS_2 film itself. Studies of the film away from cracks using AFM observed the presence of characteristic steps. For instance, in AFM frames of such film away from cracks (Fig. 6, *b*) the steps, made by WS_2 layers, are well visible. Steps height is 7–8

angstrom, and within error margin it matches the thickness of WS_2 layer from the table. Such film covered the areas on the sample of 2×2 mm size and was located in the places around electrodes, corresponding to temperature from 1050 to 1150°C.

To observe the parameters of CVD synthesis of the created setup, providing the combined synthesis of films, consisting of MoS_2 and WS_2 crystallites, the additional series of experiments was performed. For that purpose the crucibles with MoO_3 and WO_3 were simultaneously heated to temperatures of about 800−900°C, while crucible with sulfur — to temperature of 140°C. The resulting film consisted of combination of thin crystallites of triangular shape and crystallites of irregular shape. SEM image of such film is presented in Fig. 7, *a*. The performed Raman spectrometry study (Fig. 7, *b*) revealed the expected presence of two phases: MoS_2 and WS_2. Based on results, observed during early mentioned experiments, on lack of the direct formation of MoS_2 on Si(111) surface using the proposed technique, and based on successful results of regular triangular-shaped WS_2 crystallites synthesis, it can be assumed that triangular crystallites are WS_2 crystals, while irregular-shaped crystallites — MoS_2 crystals. It should be noted that presence of overlapping crystallites of MoS_2 and WS_2, as on the film synthesized using the developed technique, can be potentially used at creation of devices based on WS_2/MoS_2 heterojunction. Determination of number of WS_2 and MoS_2 layers in the resulting heterostructure and study of the electronic properties of grown WS_2/MoS_2 films are of significant interest and have been left for further studies.

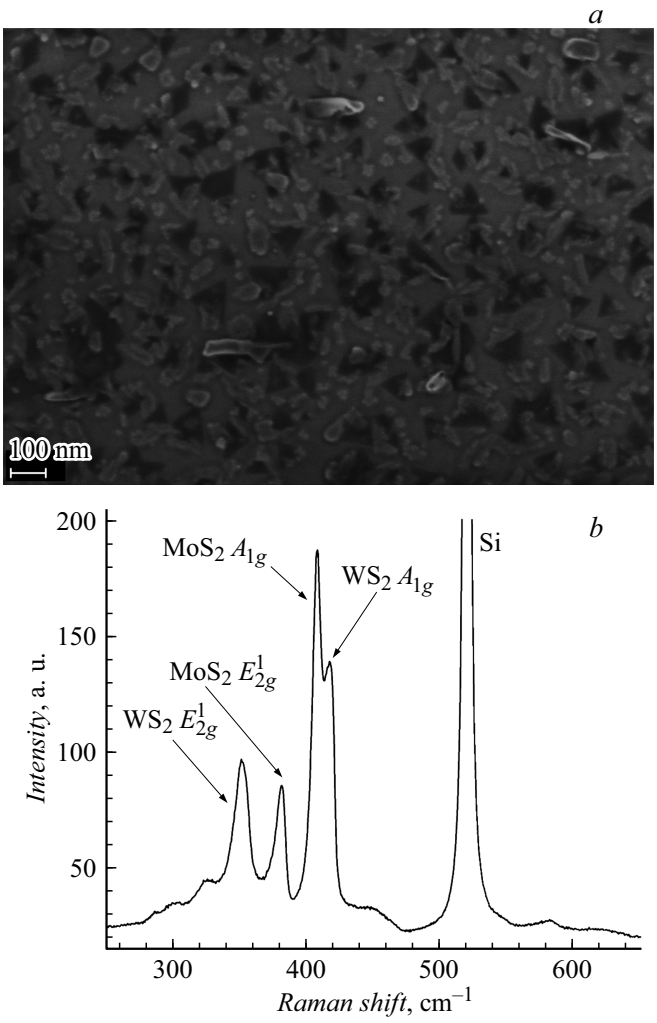

Figure 7. *a* — SEM image of WS_2 and MoS_2 crystallites film; *b* — Raman spectrum of the resulting film, where the specific lines of WS_2 and MoS_2 are visible.

Conclusion

As a result of the study we developed a new type of technique of CVD synthesis of nanostructured coatings of MoO_2, MoS_2, WS_2, differed by use of quick independent heating of each precursor and substrate, providing simultaneous implementation of the wide range of temperatures on the substrate, as well as providing opportunity of perform AFM measurements between the synthesis stages directly in reaction chamber without necessity of sample removal. Parameters of synthesis of films, consisting of vertically aligned plate crystallites of both pure MoO_2 and regular MoO_2, covered with a thin layer of MoS_2, were empirically observed. Dependence of these crystallites surface density from substrate temperature was observed. CVD process parameters, with which WS_2 film is a continuous film with a large cover area (2×2 mm) and with which the film grows as separate crystallites of regular triangular shape, were observed. Conditions of simultaneous synthesis of MoS_2 and WS_2 as WS_2 crystallites of regular triangular shape and MoS_2 crystallites without strict face were defined. Such overlapping crystallites can be used in devices based on WS_2/MoS_2 heterojunctions.

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Conflict of interest

The authors declare that they have no conflict of interest.

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