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Two-Dimensional and Screw Growth of MoS₂ Films in the Process of Chemical Deposition from the Gas Phase

R. I. Romanov^{a,*}, D. I. Myakota^a, A. A. Chuprik^a, S. M. Novikov^a,
Yu. Yu. Lebedinskii^a, A. G. Chernikova^a, and A. M. Markeev^a

^a Moscow Institute of Physics and Technology (State University), Dolgoprudny, 141701 Russia
*e-mail: romanov.ri@mipt.ru

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Abstract—The method of deposition from the gas phase is applied to the synthesis of thin films of molybdenum disulfide. It was established that varying the rate of temperature rise in the course of the synthesis affects the character of growth and the structure of the layers formed. With a decrease in the rate of temperature rise, a transition from standard two-dimensional to screw growth of MoS₂ films is observed. MoS₂ films produced as a result of screw growth have a high density of edge states, which makes them promising for use in catalysis.

Keywords: molybdenum disulfide; chemical deposition; gas phase; thin films; CVD

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On recent years molybdenum disulfide (MoS₂) has attracted a great deal of attention of researchers due to the possibility of its use in electronics, catalysis, and in the creation of fuel cells [1–3]. Thin films consisting of one or several MoS₂ monolayers are of particular interest. The possibility of producing such films by the relatively simple method of mechanical exfoliation is explained by the layered structure of MoS₂, due to weak van der Waals interatomic bonds between the series of Mo and S. The use of the method of mechanical exfoliation, however, is limited due to the small size of the crystalline MoS₂ domains. Another common method of synthesis that can be used to produce MoS₂ on an industrial scale on large substrates is chemical vapor deposition (CVD) using sulfur and various molybdenum compounds, primarily MoO₃, as precursors [4–7]. In this way, monolayer films containing crystal domains with sizes up to the millimeter level were obtained [6]. The films to be grown are characterized by a basic orientation (the basal planes are parallel to the substrate), which is most in demand in electronics. However, for use in catalysis, amorphous films [8] or films with a crystal structure with an edge orientation (basal planes perpendicular to the substrate) [9] are required. Such films have a high

density of catalytically active states, which in the case of crystalline MoS₂ are on the edges of the base planes.

In this paper, we report on the possibility of screw growth of MoS₂ films in the CVD. Films grown in this way have a basic orientation, but a high density of catalytically active (edge) states. Therefore, they can be promising for catalysis. It was previously reported that the shape and size of the crystalline domains of MoS₂ differ significantly depending on the synthesis parameters, such as the ratio of S and MoO₃ concentrations in the gas phase [10], the temperature of the precursors [11]. In this case, the transition from the standard two-dimensional growth of MoS₂ with a basic orientation to screw growth is achieved by changing the synthesis parameter such as the rate of temperature rise in the CVD. In the paper, we study the effect of the rate of temperature rise on the structure of MoS₂ films.

EXPERIMENTAL

The growth of MoS₂ films was carried out in a three-zone tube furnace HZS-1200 (Fig. 1a) (Carbolite Gero) in an argon atmosphere (99.9999%). The inner diameter of the tube was 32 mm. A crucible with MoO₃ powder

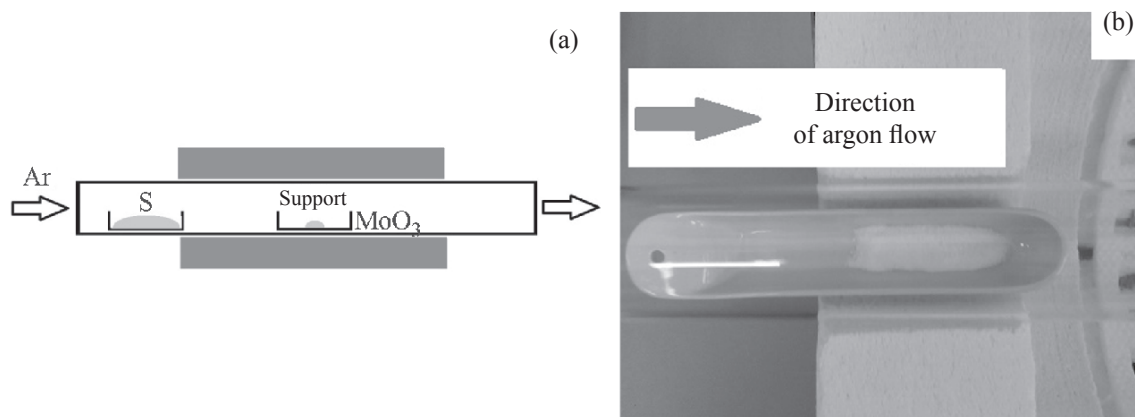


Fig. 1. Argon supply scheme, (a) the location of the crucibles and the substrate in the furnace; (b) photograph of the crucible with S located at the exit of the furnace.

(99.999%, Sigma-Aldrich) was placed in the center of the furnace. The crucible with powder S (99.99%, Sigma-Aldrich) was placed at the exit of the furnace from the side of the argon supply (Fig. 1b). The weight of MoO₃ powder was 3 mg, the weight of powder S was 350 mg. Sapphire plates with the (0001) orientation were used as substrates, which were pre-cleaned sequentially in acetone, isopropyl alcohol, and deionized water in an ultrasonic bath, and also were annealed in air at 1000°C for 1 h. The size of the substrates was 20 × 10 × 0.65 mm. Substrates were placed over a crucible with MoO₃. Before the start of the deposition, argon was passed through the furnace at a rate of 150 standard cm³ min⁻¹ for 1 h.

At the first stage of the growth, the central zone of the furnace was heated to a temperature of 300°C. The zone in which the crucible with S was placed was heated to a temperature of 200°C. Under such conditions, the furnace was held for 10 min. In the second stage, the central zone was heated to a 700°C, and the zone in which the crucible with S was placed to 600°C. Under these conditions, the oven was also held for 10 min. At the third stage, the central zone was cooled to 570°C and held at this temperature for 3 min. The substrate with the deposited film was removed from the furnace after cooling to room temperature. At the beginning of the second stage of the process, the argon feed rate was reduced from 150 to 10 standard cm³ min⁻¹.

The growth of films was carried out in two modes, which differed in the rate of temperature rise in the second stage of the process. In mode 1, the specified value of the rate of temperature rise was 40 deg min⁻¹, in mode 2, it

was 50 deg min⁻¹. In each mode 5 samples were made and tested. The actual rate of temperature change was determined graphically. For this, the plots on the graphs of the process temperature vs. time, corresponding to the temperature rise in the second stage of the process, were approximated by a linear dependence (Fig. 2). The process temperature was measured using a thermocouple installed in the central zone of the crucible with MoO₃ powder. The actual values of the rates of temperature rise were 43 ± 2 and 54 ± 3 deg min⁻¹ for modes 1 and 2, respectively.

The chemical composition of the grown films was studied by X-ray photoelectron spectroscopy (XPS) using a Theta Probe spectrometer (Thermo Scientific) with

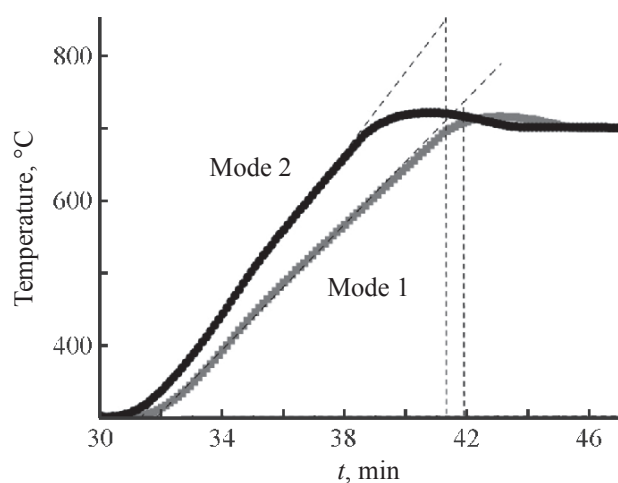


Fig. 2. Typical temperature curves in the central zone of a crucible with MoO₃ powder as a function of time for the two modes under study.

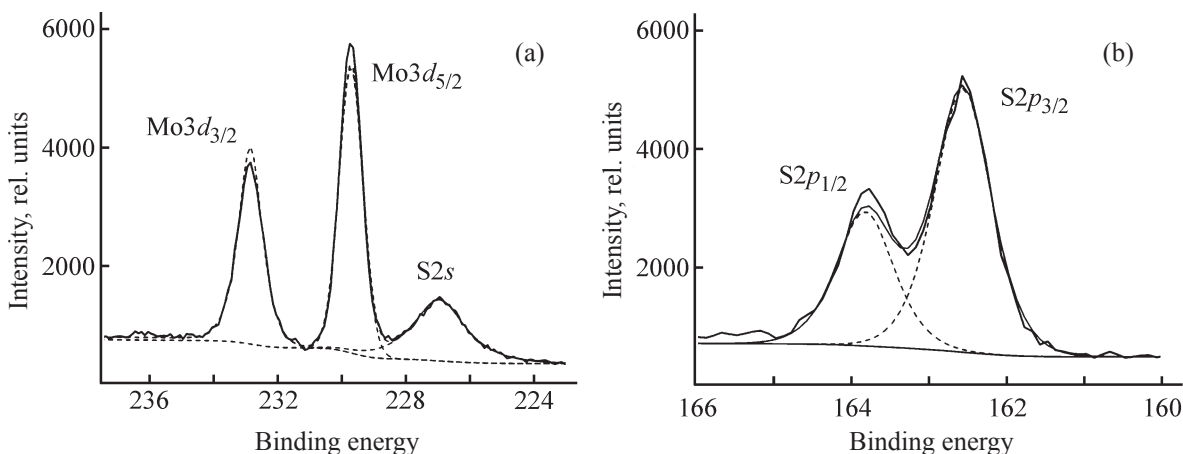


Fig. 3. XPS spectra of (a) Mo3d and (b) S2p lines obtained from film grown in mode 1.

monochromatic AlK_{α} radiation (1486.6 eV). The energy scale of the spectrometer was calibrated using the $Au4f_{7/2}$ line with a binding energy $BE = 84.0$ eV.

The surface morphology of the films was studied by atomic force microscopy (AFM) in the semicontact mode using an Ntegra microscope (NT-MDT) and HA-NC (NT-MDT) series cantilevers with a radius of curvature less than 10 nm. For more morphology visualization, the method of phase imaging in the semicontact AFM mode was used [12, 13]. Due to the possible heterogeneity of the grown layers, the morphology was estimated both in the central zone of the samples and at a distance of 7 mm from the center.

The structural features of the obtained films were studied by Raman spectroscopy using a LabRAM Evolution spectrometer (Horiba Scientific) equipped with a laser source with a wavelength of 632.8 nm and a spectral resolution of 1 cm^{-1} . The diameter of the laser focusing spot was $1\text{ }\mu\text{m}$.

RESULTS AND DISCUSSION

Figure 3 shows the XPS spectra of the high resolution of the Mo3d and S2p lines by the example of a film grown in mode 1. It can be seen that the Mo3d line (Fig. 3a) can be represented as a single doublet with a binding energy of Mo3d_{5/2} $BE = 229.8$ eV, and the S2p line (Fig. 3b) is in the form of a single doublet with the position S2p_{3/2} $BE = 162.6$ eV, which corresponds to the formation of MoS₂ [14]. It should be noted that the presence of an additional peak in the region of lower binding energies in Fig. 3a is associated with the presence of the S2s line in this

spectral region. Similar spectra were obtained in the case of analyzing films grown using mode 2. The calculation of the relative atomic concentrations of S and Mo against the intensities of the XPS lines obtained taking into account the elemental sensitivity factors showed that the ratio of atomic concentrations of S and Mo is about 2.05 in both cases. Thus, the formation of MoS₂ in the discussed CVD using both modes is confirmed.

An analysis of the AFM images (Figs. 4, 5) shows the continuity of the grown films in the central zone and the growth of individual domains at a distance of 7 mm from the center in both growth modes. At the same time, the structure of MoS₂ films grown in modes 1 and 2 has qualitative differences. The result of using a lower rate of temperature rise (mode 1) is a screw package of basal planes. The height of the steps of this package, determined by the profiling method (Figs. 4a, 4c), is about 0.6 nm, which, according to [15], is the thickness of a single MoS₂ monolayer. At the same time, the standard triangular or also hexagonal shape of the domains lying at the base of the screw structures described in [11] can be traced. In the central zone of the film (Figs. 4a, 4b), the height of the latter reaches 6 nm, which corresponds to the total number of monolayers ≈ 10 . Despite the large number of layers in each screw structure and the observed continuity of the film, the layers do not coalesce into a single domain. As a result, the obtained screw package is characterized by a high density of edge states. At a distance of 7 mm from the center (Figs. 4c, 4d), the density of the edge states, however, decreases, since the number of layers in each screw structure are reduced. The height of the screw

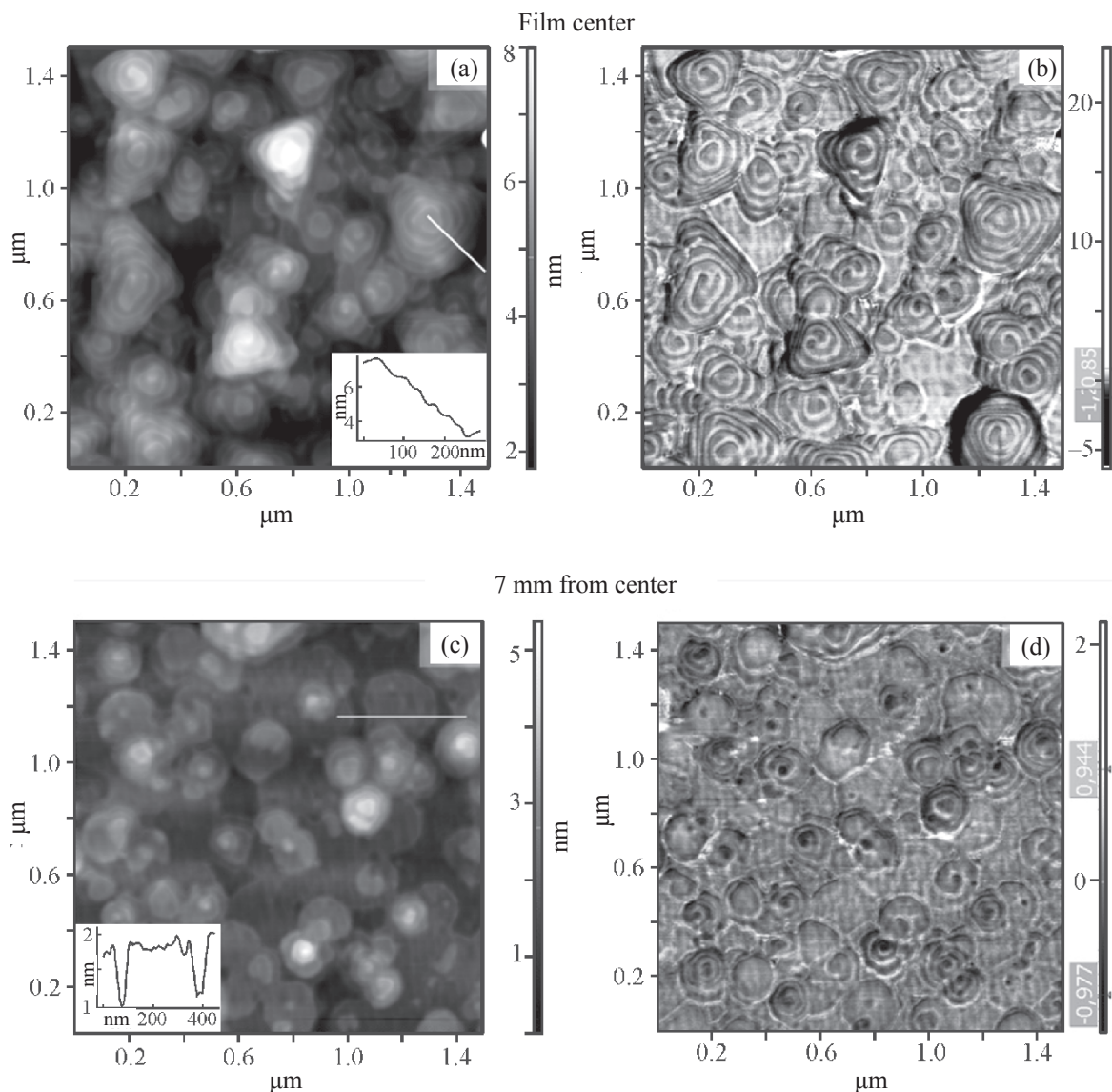


Fig. 4. (a, c) AFM images obtained in topography mode and (b, d) phase contrast (a, b) in the central region and (c, d) at a distance of 7 mm from the center of MoS₂ films formed in mode one. Inserts in Figs. 4a, 4b correspond to sections of morphology along white lines.

structures is 0.6–2 nm. Note that the lateral dimensions of the bases of the screw structures are 100–300 nm.

Increasing the rate of temperature rise (mode 2), as follows from Figs. 5c, 5d, leads to the standard two-dimensional growth of triangular MoS₂ crystal domains at a distance of 7 mm from the center of the sample. Domains are randomly oriented. The domain thickness is 1.2–3 nm, which corresponds to 2–5 MoS₂ monolayers. In Figs. 5c, 5d, objects with a size of less than 50 nm are also clearly distinguishable (one of them is indicated by an arrow), which can be nuclei of the formation of MoS₂ domains. In the central region of the sample, according to Figs. 5a, 5b, the accretion of domains occurs into a continuous film.

To confirm the structural features of the grown films that were determined using AFM, the Raman spectra were analyzed (Fig. 6). First of all, it should be noted that the spectra contain characteristic peaks corresponding to the vibrational modes A_{1g} and E_{2g}^1 of atoms in MoS₂, which confirms the formation of MoS₂ in both modes. In the case of mode 2, in Raman spectra the shifts are about 405 and 384 cm⁻¹ for A_{1g} and E_{2g}^1 , respectively, the difference of the shifts of the characteristic peaks is 21 cm⁻¹. It is known that the latter depends on the number of monolayers in the MoS₂ film and varies from 26 to 19 cm⁻¹ with a decrease in the number of monolayers from 20 to 1 [6]. The value 21 cm⁻¹ obtained for mode 2 corresponds to two mono-

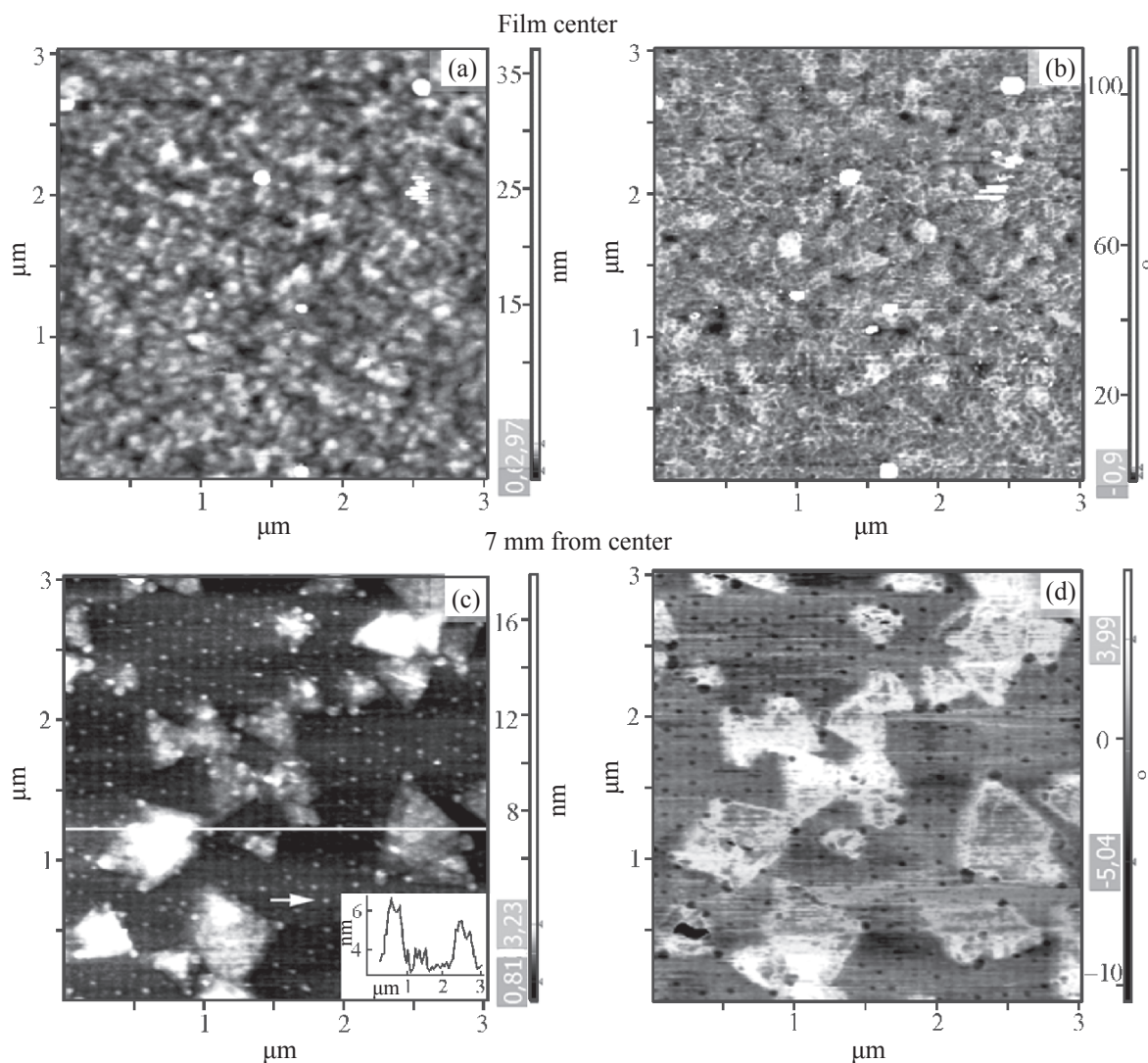


Fig. 5. AFM images obtained (a, c) in topography mode and (b, d) phase contrast (a, b) in the central region and (c, d) at a distance of 7 mm from the center of MoS₂ films formed in mode 2. Insert in Fig. 5c corresponds to the cross section of morphology along the white line.

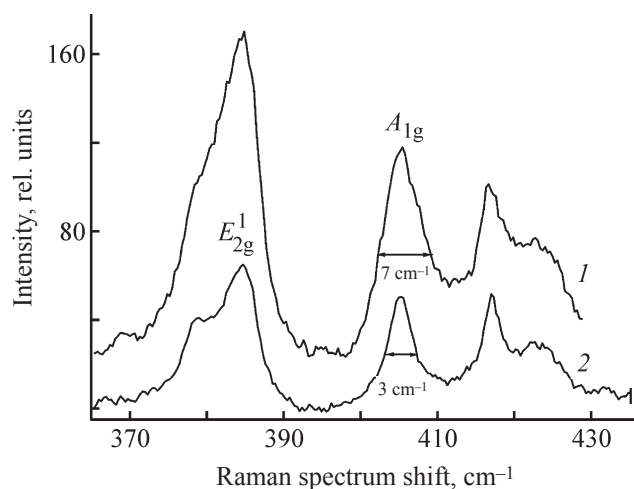


Fig. 6. Raman spectra of MoS₂ films grown in (1) modes 1 and (2) 2.

layers of MoS₂, which is consistent with the results of the AFM study. On the Raman spectrum of a film grown in mode 1, firstly, an increase in the difference in shifts of characteristic peaks (23 cm⁻¹) is observed, which corresponds to a larger number of monolayers. Secondly, there is a significant broadening of the characteristic peaks, which may be associated with different numbers of monolayers in different screw structures located in the analysis zone. Indeed, the full width at half maximum, FWHM) of the peak responsible for the oscillatory mode A_{1g} for mode 1 is ≈7 cm⁻¹, while for mode 2 FWHM ≈ 3 cm⁻¹. Thus, the results of the analysis of the Raman spectrum and the data obtained using AFM indicate that in mode 1, screw growth of MoS₂ films is realized. Note that a further decrease in the rate of temperature rise caused only an insignificant change in the size of the crystalline domains of MoS₂.

CONCLUSIONS

The variation of the temperature-time regime in the CVD process of MoS₂ growth allows the transition from standard two-dimensional growth of thin films to screw growth. Two-dimensional growth of thin films (3–5 monolayers) of MoS₂ was carried out at a temperature of 700°C and a furnace heating rate of 54 ± 3 deg min⁻¹, while reducing the heating rate to 43 ± 2 deg min⁻¹ resulted in a screw growth of structures. In these structures, the absence of accretion of the basal planes contained in them was observed up to the thickness of the structures of 10 nm and the continuity of the film visible by means of AFM. As a result, a high density of edge states, potentially demanded in catalysis, was provided.

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CONFLICT OF INTEREST

The authors declare no conflict of interest requiring disclosure in this article.

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