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XRD analysis of nanolayered molybdenum disulfide obtained by sol-gel technology

Abstract. The deposition of molybdenum disulfide by sol-gel technology was investigated. Initial mixture for the synthesis was prepared from ultrafine powders of metals and elemental sulfur. Synthesis was performed slowly during 2 h by precipitation of the molybdenum hydroxide from aqueous 0.001M solution of $MoSO_2$ and sodium hydroxide with constant stirring. By morphology obtained layers of particles of molybdenum disulfides deposited on silicon substrate have bimodal distribution: from 0.1 to 0.2 μm with a maximum at 0.15-0.18 μm; and from 0.4 to 5.0 μm with a maximum at 3.0 μm. It was established that obtained molybdenum oxide hydroxide particles do not coagulate within 48 h, which is associated with the formation of micellar positively charged particles. According to the data of X-ray diffraction and Raman spectroscopy disulfide particles have a layered structure, and the main phase is a hexagonal disulfide with a space group of symmetry P63 / mmc. By X-ray images it was established that increasing the sulfur content in the mixture in the synthesis of nanostructured molybdenum disulfide is reflected on reducing the intensity and number of reflections phase, as well as on reducing the rate and the maximum temperature of combustion. Upon sulfur excess higher than 15% by weight, the phase of mainly hexagonal molybdenum disulfide was observed in the product. By estimation of zeta potential, the value of zeta potential was 54 mV, clearly indicating that the particles obtained in aqueous suspension are not coagulating due to the predominance of the processes of repulsion of the particles.
Key words: sol-gel technology, molybdenum disulfide, XRD-analysis, Raman spectroscopy.

Introduction

Molybdenum disulfide is used in areas such as photovoltaic cells, rechargeable batteries, and solid lubricants. This is due to their optical, electrochemical and mechanical properties. Molybdenum disulfide has a hexagonal crystal lattice in which metal layers are arranged between two layers of sulfur connected by weak van der Waals forces [1]. Because of the structural features of the crystal lattice, it is interesting in the applied aspect.

Due to the widespread in nature as molybdenite, MoS_2 has been one of the most studied layered transition metal dichalcogenides (TMDCs). Monolayer MoS_2 is a semiconductor with a direct bandgap of 1.8 eV [2]. This property of MoS_2 is inspiring, which will largely compensate the weakness of gapless graphene, thus making it possible for 2D materials to be used in the next generation switching and optoelectronic devices. Thus far, MoS_2 has achieved primary progress in the following fields, including energy conversion [3] and storage [4] and hydrogen evolution reaction (HER) [5]. Additionally, MoS_2 with odd number of layers could produce oscillating piezoelectric voltage and current outputs, indicating its potential applications in powering nanodevices and stretchable electronics [6].

At present, in the world, intensive work is aimed at the study of photoconductive materials for use in photovoltaic solar energy converters and other optoelectronic devices. In this aspect, molybdenum disulfide (MoS_2) is a promising active component of such materials, because it has a broad absorption spectrum in the range from 200 to 1000 nm, and also has a high photo – and corrosion resistance [7].

Due to the particular optical and electrical performance of TMDCs, as one of the most typical existing TMDCs, MoS_2 itself has evolved into a vast studying topic, gradually finding its applications in many related areas, such as transistors [8], photodetectors [9], solar cells [3], etc.

Therefore, the fabrication of hybrid structures based on 2D materials by taking advantages of the individual component is one of latest research trends. The ultimate goal is to synthesize more superior composites, achieving synergistic effect or structural reinforcement.

Early in 2011, Yandong Ma's group has calculated that the binding energy of per C atom binding to MoS_2 is A 23 meV and the forming interlayer spacing between graphene and by MoS_2, band structure of graphene could be largely preserved in this hybrid structure while introducing a small bandgap of 2meV which was almost negligible [10]. Further analysis indicated that this band gap was tunable by varying the interlayer spacing, highlighting the prospect in designing of devices with tunable bandgap and high electron mobility simultaneously. In 2011, A. K. Geim proposed "van der Waals heterostructures" on Nature [12], showing a landscape for future development of 2D hybrid structures. Many challenges were accomplished afterwards, pushing devices into real practical applications. J. C. Grossman and his co-workers confirmed the feasibility by studying the performance of 1 nm-thick solar cell based on MoS_2/graphene through the first principles calculations [11]. First, MoS_2 like TMDCs monolayers could absorb 5 -10% of incident sunlight within 1 nm in thickness, exceeding that of traditional semiconductors (GaAs and Si) more than one order of magnitude.

In addition, A type-II Schottky junction within 1 nm which would greatly facilitate separation and transport of carriers in the stacking interfaces was constructed, exporting a high power conversion efficiency (PCE) up to ~1%. Moreover, MoS_2/graphene solar cell demonstrated a power density of 0.25 – 2.5 mW/kg, which were higher by approximately 1 – 3 orders of magnitude than the best existing ultrathin solar cells [11]. Further experimental observation proved the ultrafast interfacial charge transfer in TMDCs stacking structures, ensuring the effective charge collection and utilization in later circuits [12], opening up the development for light detection and harvesting in atomically thin devices.

Band engineering of MoS_2, achieving composite constructions with superior electrical performance and tunable band structure, is a leading topic in the near future. Therefore, to put the existing flexible optoelectronic and energy storage devices into practical and industrial applications, the most feasible method and technology are needed to be further investigated [13].

Experimental procedure

In this work, molybdenum disulfide obtained by sol-gel technology was considered as an investigated material. Optical measurements were made by an optical microscope Leica DM 6000M, which has a resolution of 200 nm, the maximum magnification of 1500 and is equipped with high-resolution digital camera Leica DFC Twain.

The quality and uniformity of the surface condition of the obtained samples were studied using Raman spectroscopy. The Raman spectra of obtained samples were studied on NT-MDT NTEGRA by using blue laser light with a wavelength of λ = 473 nm and a spot diameter of 2 μm. Full range of Raman / fluorescence was recorded at each point of the test sample, followed by software processing. Due to the high quality of the optical system, two- and three-dimensional distribution of the spectral characteristics of the sample could be examined with a spatial resolution close to the theoretical limit.

To solve the problems of X-ray diffraction and X-ray analysis of the materials, X-ray diffractometer DRON-7 with a wavelength $\lambda_{CuK\alpha}$ = 1.54178 Å was used.

The phase composition of molybdenum disulfide was analyzed at room temperature using a diffractometer Shimadzu XRD-7000S, type of anode – Cu, focus -0.4x 12 mm, and a maximal power –2,7 kW, and scan rate -1°/min with a 0,002°. Decoding of the data was performed using the database of JCPDS X-ray diffraction.

Experimental part

Synthesis of molybdenum sulfide was produced by slow precipitation (within 2 h) of molybdenum hydroxide from the 0.001 M $MoSO_2$ aqueous solution and sodium hydroxide solution, with constant magnetic stirring. As a result, following chemical processes were proceeded sequentially:

$$MoSO_2 + 2NaOH = Mo(OH)_2 \downarrow + Na_2SO_2$$
$$Mo(OH)_2 + O_2 = H_2O + MoOOH \downarrow$$

Upon completion of the synthesis, a stable suspension of oxide hydroxide molybdenum was formed. Qualification of sedimentation stability of

the slurry revealed that the obtained particles of oxide hydroxide molybdenum were not coagulated for 48 hours. This is due to the formation of micellar positively charged particles. Evaluation of zeta potential determined by a moving boundary has shown that the value of the zeta potential is 54 mV. The value of zeta potential clearly indicates that the processes of coagulation are not characteristic for the obtained particles in aqueous suspensions due to the predominance of the processes of repulsion between them [14].

In Figure 1, a micrograph of obtained layers of molybdenum disulfide deposited on a silicon substrate is presented. Treated disulfides are nanolayer powder and the particles of the obtained samples have a spherical shape. Particle size distribution has bimodal distribution: from 0.1 to 0.2μm with a maximum at 0.15 – 0.18 μm; from 0.4 to 5.0 μm, with a maximum of 3.0 μm.

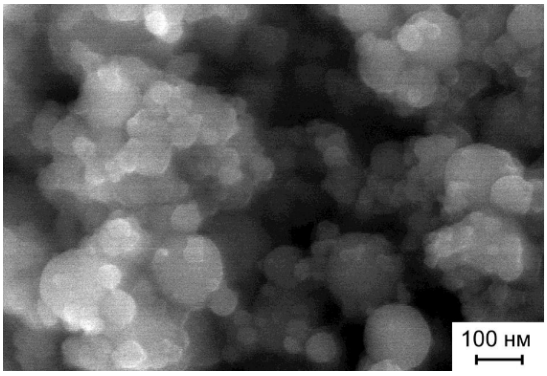

Figure 1 − A micrograph of molybdenum disulfide particles deposited on a silicon substrate, x20.

In Figure 2, the Raman spectrum of molybdenum disulfide is shown. The increased intensity of the peaks in the spectrum of a molybdenum disulfide indicates an elongated crystal structure. The peaks at ~ 388 and 407 cm^{-1} correspond to the vibration modes $E^1_{2g}$and E_{1g} .

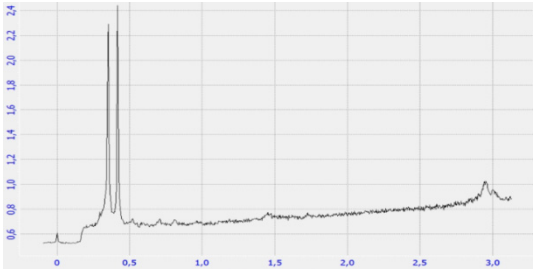

Figure 2 − Raman - spectrum of molybdenum disulfide on a silicon substrate.

In Figure 3, the X-ray diffraction analysis of samples at various excess of sulfur in the initial mixture with the powder of molybdenum is shown. It can be seen that in the composition of particles molybdenum oxide, oxide hydroxide molybdenum and predominant content of molybdenum sulphide phase are present and the main phase is a hexagonal disulfide with a space group of symmetry P63 / mmc. Molybdenum disulphide with a hexagonal crystal lattice is marked with characteristic reflexes of planes (002), (101), (103), (006), (110), (108). In addition, phase of rhombohedral MoS_2 is present in the sample. Unfortunately, according to XRD phase of elemental sulfur is not determined, this is connected either with its small amount, or with its X-ray amorphous state. From the XRD, it is shown that with increasing the excess of sulfur, the intensity and number of phase reflections are reduced and in the sample with 15% excess of sulfur it is not observed, which indicates the completeness of the conversion of initial mixture into the molybdenum disulfide.

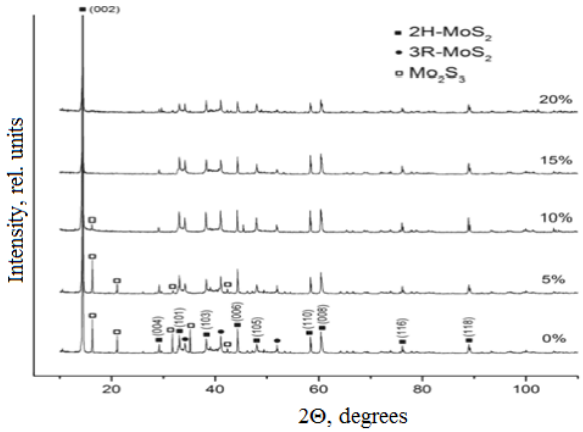

Figure 3 − XRD analysis of the samples at various excess of sulfur in the initial mixture with the powder of molybdenum.

Taking into the account that the process of synthesis takes place on the surface of the particles, the released sulfur gradually blocks surface of the particles. As a result, a process of gradual deceleration of the formation of molybdenum sulfide is observed. As a result, the particles are formed comprising a core of oxide hydroxide molybdenum covered by molybdenum sulfide film, and on the surface of which elemental sulfur is. This hypothesis is partially confirmed by X-ray diffraction data of the particles extracted from the solution, the results of which are shown in Table 1.

Table 1−X-ray diffraction data for the MoS_2– particles

Phase	Phase content, % wt	The size of coherent scattering, nm
MoS_2	68	30
MoO_2	22	123
$MoOH_3$	10	-

The increased peak intensity in the (002) on diffraction patterns of molybdenum disulfide indicates an elongated crystal structure (Figure 4). The results of X-ray diffraction analysis indicate that at least 95% of metal disulphide is contained in the final products of synthesis.

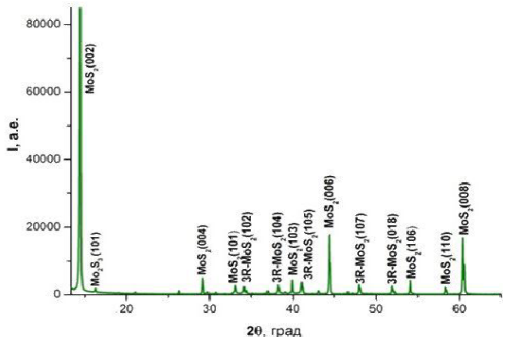

Figure 4 − X-ray image of molybdenum disulfide.

According to XRD data, the disulfide particles have an extended form, a layered structure, and the main phases are hexagonal disulfide with space group of symmetry P63 /mmc. Parameters of crystal lattice for hexagonal MoS_2 are a = 3.161 Å, c_1 = 12.27 Å, and for rhombohedral c_2 = 18.35 Å.

From the obtained data, it is clear that mostly molybdenum sulfides and disulfides with the presence of residual amounts of molybdenum oxide are formed by the proposed method of synthesis. This composition of obtained samples has a possibility to be used for photovoltaic cells.

Conclusions

1. As a result of the proposed procedure for obtaining molybdenum sulfides by sol-gel technology, sulfides and molybdenum disulfides with the presence of residual amounts of molybdenum oxide are formed.

2. The obtained disulfide particles have an extended form, a layered structure, and the main phases are hexagonal disulfide with space group of symmetry P63 / mmc.

3. An increase of the sulfur content in the mixture during the synthesis of nanostructured molybdenum disulfide reduces the rate and maximum temperature of combustion. Upon excess of more than 15% sulfur by weight mainly the phase of hexagonal molybdenum disulfide is observed in the product.

4. The value of the electrokinetic potential is 54 mV, according to zeta potential it clearly indicates that the processes of coagulation are not characteristic for the obtained particles in aqueous suspensions due to the predominance of the processes of repulsion of the particles.

MoS_2 has been triggering a new wave of research and far from being exhausted. Recently, stable preparation high quality MoS_2 in large area for applications in industrial-scale is still challenging. Research on van der Waals heterostructures reassembling has emerged over the past three years, while the interfacial contact between each building layer needs to be further optimized. In addition, the band engineering of MoS_2, achieving composite constructions with superior electrical performance and tunable band structure, is a leading topic in the near future [13].

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