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Nanostructured Films of Semiconducting Molybdenum Disulfide Obtained Through Exfoliation-Restacking Method

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Preparing MoS_2 films in mild conditions, using deposition of suspended MoS_2 nanoplatelets onto the substrate is described. For this purpose, the nanosized MoS_2 particles were obtained via restacking of MoS_2 single layers produced by chemical exfoliation of bulk MoS_2 crystals in liquid media. X-Ray diffraction study of the films showed that the basal planes of MoS_2 crystallites are mainly oriented in the plane parallel to the substrate. Atomic force microscopy examination revealed the dependence of the film surface topography, as well as the roughness characteristics on the film thickness, which varied in the range of 0.03-2.2 μm. Optical absorption spectra of the obtained MoS_2 films were found to contain the same absorption bands as the spectra of thin natural MoS_2 single crystals. Dark conductivity of the films was determined to be ~ 10^{-3} S·cm^{-1} at 300 K. The present MoS_2 films were found to be photosensitive in the range of 300-800 nm, providing the maximum value of photocurrent under photoexcitation at ~ 440 nm.

Keywords: Molybdenum Disulfide, Exfoliation, Thin Films, Surface Structure, Photoconductivity.

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1. INTRODUCTION

Thin-film materials are widely used in modern electronics. The problems of obtaining the semiconductors in the film form in mild conditions is thus the subject of current interest. It can be a major challenge to find conditions for preparing the films from insoluble and non-volatile compounds like molybdenum disulfide. Indeed, MoS_2 is a semiconducting material, which was shown to hold promise for designing TFTs [1], photoactive electrodes [2] and solar cells characterizing by a high solar-to-electric energy conversion efficiency [3]. The material is available in nature as a mineral, photocorrosion-resistant and non-toxic. However, the methods previously tested for the synthesis of MoS_2 films, including CVD and bath deposition techniques, electrodeposition, and sulfiding the precursors, often results in law-ordered films or requires the high temperature conditions [4].

2. FILMS ASSEMBLING

An approach here presented implies the use of peculiarities of MoS_2 crystal structure to obtain the colloid-like fragments of the crystals in liquid media and to assemble then these fragments in the films on the substrate [5, 6].

From the structural standpoint, MoS_2 is a layered compound containing triatomic-thick S-Mo-S layers bound up each to other by van-der-vaals bonds in the bulk crystals. Reductive lithiation of bulk crystalline MoS_2 and following hydration of the resulting layered compound $Li^+(MoS_2)^-$ was shown to produce the liquid-phase dispersions containing $(MoS_2)^{x-}$ single layers separated by solvent molecules: $[Li^+ + (MoS_2)^{x-} + (1 - x)OH^-]_{aq}$ [7]. These single layers can further be arranged in the ultra-dispersed neutral MoS_2 particles, containing from several to several tens monolayers of MoS_2, as evidenced by HRTEM [8]. Because of two-dimensional character of MoS_2 structure, the produced particles are anisotropic in shape and their lateral dimensions are larger than the side ones. Such morphology should favor uniform orientation of the particles depositing on the substrates and facilitate forming the films.

The films with various thicknesses (d = 0.03–2.2 μm) were prepared by layer-by-layer putting the suspensions of dispersed MoS_2 particles in organic solvents onto the polished quartz plates of the size of 2.0 x 2.5 cm. Then, the films were dried at 20ºC and heated at 150ºC in vacuum for 2 hours. For electrical and photoelectrical measurements, surface Cu electrodes of the width and length of 1 and 15-18 mm, respectively, were deposited by vacuum sputtering onto the films within the distance of 2 mm from each other.

3. AFM AND XRD CHARACTERIZATION

Powder X-Ray diffraction study of MoS_2 films obtained from suspensions showed that their patterns contain broad reflections of *00l* series, which dominates over the other reflections (Fig. 1). This is consistent with preferable orientation of the basal surfaces of MoS_2 particles in the plane parallel to the substrate with the crystallographic *c*-axis of the particles being perpendicular to the substrate. Drying the films at 150ºC in vacuum leads to noticeable narrowing of the *00l* reflections, that is a sign of increasing the crystal-

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linity and uniformity of interlayer distances in the particles constituting the film. Since this treatment doesn't lead to increase of *100* and *10l* reflections in intensity, one can conclude that structurization of the particles in the films is not accompanied by their misalignment with respect to the substrate.

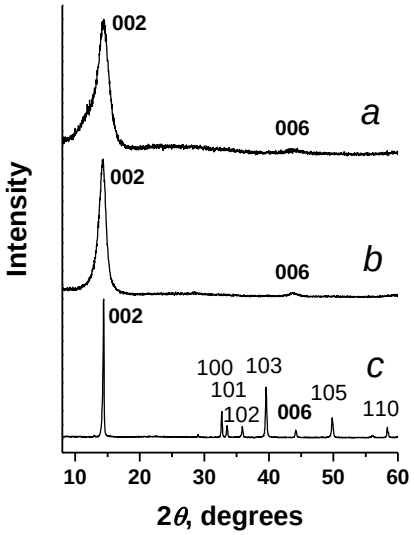

Fig. 1 – XRD patterns of the prepared MoS_2 film after deposition onto substrate (*a*) and after drying at 150°C (*b*) as well as the pattern of crystalline MoS_2 (*c*).

AFM scans were performed to examine the surface topography of the obtained films. Fig. 2 shows 3D images of the surface structure obtained for the films of different thickness (0.03, 0.06 and 1.3 μm), using relatively large surface areas of about 14x14 μm for the analysis. It can be seen from these data that, on increasing the thickness, the surface of the films more and more deviates from the flat geometry and contain more step-layer pyramid-like nanocrystalline elements, possessing clearly pronounced faces and differing from each other in sizes. In the film with thickness of 1.3 μm, these elements, reaching 560 nm in height, cover all the surface. The tendency of surface microrelief to be more developed for the thicker films is consistent with the observed changes in roughness parameters of the films, including the peak to peak value (R_{max}), the average (R_a) and root mean square (R_q) roughness. For all these characteristics, an abrupt increase of the corresponding value upon changing the thickness from $d = 0.03$ to $d = 0.43$ μm is followed by a gradual approaching the plateau at $d > 0.43$ μm.

4. FORMATION MECHANISM OF FILMS POLYCRYSTALLINE STRUCTURE

Basing on the results of AFM and XRD studies, the following mechanism of the formation of these polycrystalline films can be proposed. The MoS_2 nanoparticles formed in restacking process contain several (3-8 and more) S-Mo-S layers, as follows from the data obtained previously [8]. Upon deposition of the first portions of suspension onto the smooth surface, the flat shape of MoS_2 particles promotes their parallel orientation with respect to the substrate plane. However, disordering of the packing is growing up on further depositions. It is caused by the nonequivalence of the thickness of the particles coming from the suspensions, so that the surface of the first deposited layer cannot be an ideal smooth substrate for the next layer. The "scarps" formed in the relief hamper deposition of the subsequent nanoparticles in the orientation parallel to the substrate. Moreover, the side surface of the "scarps" becomes the places for attaching the particles in the inclined orientation. So these side steps become the centers of "crystallization", which provides the growth of differently oriented nanocrystallites. This results in formation of densely packed step-layered structures, and their orientation with respect to the substrate plane becomes more and more chaotic with increasing the films thickness.

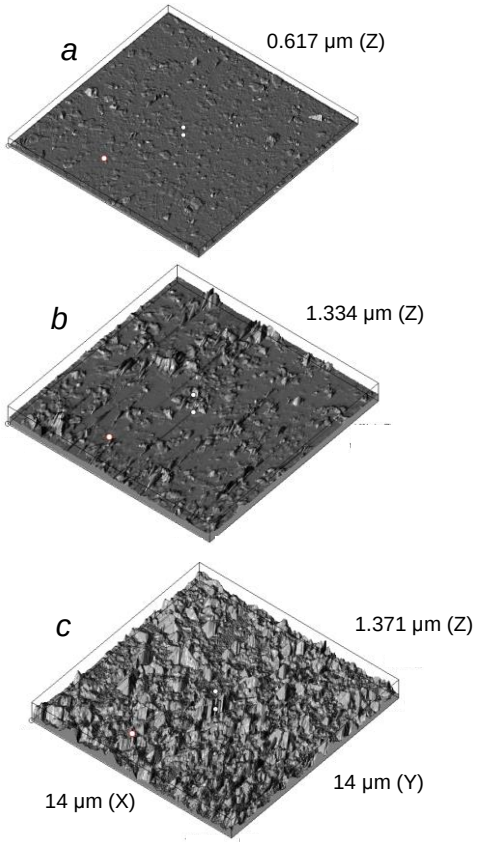

Fig. 2 – 3D images of surface topography of MoS_2 films. The film thickness is 0.03 μm (*a*), 0.06 μm (*b*) and 1.3 μm (*c*).

5. ABSORPTION SPECTRA, DARK- AND PHOTO- CONDUCTIVITY OF THE FILMS

Optical absorption spectra of dispersed MoS_2 films assembled by exfoliation-restacking method and having the different thickness (30-170 nm) were measured. According to the obtained data, the spectra are in general similar to the spectrum of single-crystalline MoS_2 and show the thresholds of absorption bands begining at ~700, ~500 and ~350 nm, corresponding to the 1-st, 2-nd and 3-rd band. (Fig. 3). However, the fine structure of absorption bands with the maxima excitonic in nature is less pronounced in the spectra of the films.

Decreasing the films thickness to 30 nm does not change the spectrum shape, but affects the value of optical absorption.

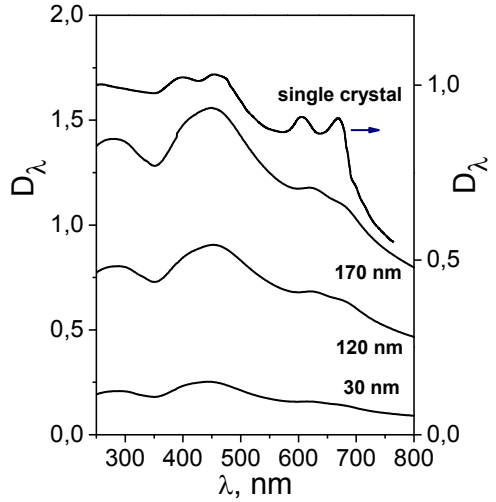

Fig. 3 - Absorption spectra of the dispersed films and single crystal of MoS_2.

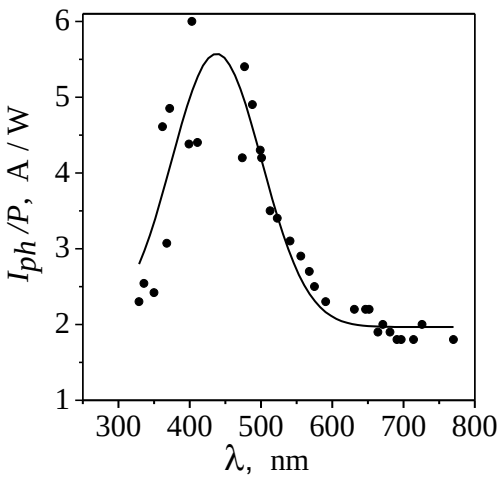

Fig. 4 - Photocurrent spectrum measured in the MoS_2 film and corrected for the light intensity (d = 0.043 μm, applied voltage U = 15 V).

Dark conductivity of the films with the thickness of 0.12-2.2 μm measured using surface-type electrodes was found to be ~ 10^{-3} S·cm^{-1} at room temperature.

Similarly to single-crystalline specimens of MoS_2, the present films were found to exhibit photoconducting properties. Spectral dependence of the photocurrent corrected for the excited light intensity is presented in Fig. 4. It can be seen that photocurrent reaches a maximum at ~ 440 nm and its position roughly coincides with the position of the second band in the absorption spectra. It means that the processes attributed to this absorption band (direct transitions from the top of the valence band and deeper levels into the conduction band) are also responsible for the photocurrent.

Thus, soft chemistry method of the preparation of thin semiconducting molybdenum disulfide films using nanocrystalline MoS_2 has been developed. Contrary to the usual high-temperature techniques, the described preparation proceeds at room temperature and is followed by annealing to 150°C. The obtained results are expected to be of interest for researchers dealing with films of various layered structure materials.

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REFERENCES

1. D. Lembke, A. Kis, *ACS Nano* **6**, 10070 (2012).
2. F.A. Frame, F.E. Osterloh, *J. Phys. Chem. C* **114**, 10628 (2010).
3. C.-J. Liu, S.-Y. Tai, S.-W. Chou, Y.-C. Yu, K.-D. Chang, S. Wang, F.S.-S. Chien, J.-Y. Lin, T.-W. Lin. *J. Mater. Chem.* **22**, 21057 (2012).
4. N. Barreau, J.C. Bernede, *J. Phys. D: Appl. Phys.* **35**, 1197 (2002).
5. T.S. Zhuravleva, E.P. Krinichnaya, O.P. Ivanova, I.V. Klimenko, A.S. Golub, N.D.°Lenenko, I.A. Misurkin, S.V. Titov, *Thin Solid Films* **520**, 3125 (2012).
6. I.V. Klimenko, A.S. Golub, T.S. Zhuravleva, N.D. Lenenko, Yu.N. Novikov, *Russ. J. Phys. Chem. A* **83**, 276 (2009).
7. R.A. Gordon, D. Yang, E.D. Crozier, D.T. Jiang, R.F. Frindt, *Phys. Rev. B* **65**, 125407 (2002).
8. A.S. Golub, V.I. Zaikovskii, N.D. Lenenko, M. Danot, Yu.N. Novikov, *Russ. Chem. Bull.* **53**, 1914 (2004).