Structural and electrochemical properties of W-Se-O layers prepared by pulsed laser pre-deposition and thermal post-treatment

A A Soloviev¹, S N Grigoriev², D V Fominski¹,³, M A Volosova² and R I Romanov¹

¹National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe sh. 31, 115409 Moscow, Russia
²Moscow State University of Technology “STANKIN”, Vadkovskii per. 3a, 127005 Moscow, Russia

E-mail: dmitryfominski@gmail.com

Abstract. Novel nanostructured thin-film coatings containing WSe₂ and WO₃ nanosheets were prepared through a simple and highly reproducible method. Pulsed laser pre-deposition of W-Se-O films on a microcrystalline graphite substrate by ablation of WSe₂ target in a mixture of Ar and O₂ gases was followed by thermal post-treatment. The influence of pre-deposition and post-treatment conditions on the structure, morphology and chemical composition of the W-Se-O films was studied. Thermal annealing at appropriate conditions of pre-deposited amorphous W-Se-O films resulted in the formation of crystalline structure consisted of nanocrystals of WSe₂ and WO₃ phases. Such structural modification significantly altered the electrochemical properties of the thin-film coatings with consequences, in particular, on their catalytic activity toward hydrogen evolution reaction in an acid solution.

1. Introduction

Recently, two-dimensional (2D) or quasi-two-dimensional (Q2D) layered transition metal dichalcogenides (TMDs) have received great attention as potential catalysts for hydrogen evolution reaction (HER) in acid solutions (e.g., Pumera et al. [1]). The active sites for HER are located along the edges of the molecular layers consisted of atomic chalcogen-metal-chalcogen sandwiches. Therefore, ultra-thin TMD nanocrystals possessing sheet-like shape are promising materials for obtaining effective catalysts of HER [2].

Unfortunately, in accordance with conclusions of Mao et al. [3] and Vrubel et al. [4], the catalytic activity of such TMD nanosheets is still limited due to the inevitable agglomeration and stacking of the liquid exfoliated nanosheets. TMD nanosheets coupled with highly conductive nanomaterials, e.g., carbon nanotubes and graphene, have been proposed by Tang et al. [5] and Mao et al. [3] to enhance the catalytic activity.

Transition metal oxides also have a layered packing of atoms in the crystal lattice and when dimensions of the oxide crystals decreased due to ultra-thin 2D/Q2D nanosheets formation the physicochemical properties of the oxides can be changed. Zhuuykov et al. [6] and Ketpang et al. [7] revealed that in contrast to "bulk" metal oxides samples, nanostructured oxides exhibit good

³To whom any correspondence should be addressed.
conductivity and improved catalytic properties in HER. Electrical properties of some metal oxide films, such as WO$_3$ films, can be modified significantly due to interaction with hydrogen [8].

For WO$_3$-S system, Wu et al. [2] revealed interesting effects when chalcogen atoms chemically interacted at elevated temperatures with WO$_3$ ultra-small particles. During the annealing of the mixture consisted of WO$_3$ and S particles, WS$_2$ shells were produced on the WO$_3$ particles surface and then peeled off to form WS$_2$ nanosheets. After the outer layer (i.e., WS$_2$ shell) peels away, WO$_3$ particles became smaller and more active than the ones with larger size, and it became easier for S to coat their outer surface to form new WS$_2$ shell. Mechanical activation of ball milling was essential factor to get close contact between S and WO$_3$ and facilitate the shell formation due to sulfurization. For WS$_2$ nanosheets catalyst fabrication, additional/special mechanical and chemical procedures should be carried out [2].

It is of great interest the preparation of the nanosheet-based thin-film catalyst by using the specific processes of phase transformation that are characteristic of chalcogenide-oxide system. The aim of this work was to develop a novel thin-film material containing nanosheets of tungsten diselenide (WSe$_2$) and WO$_3$ and to study the HER catalytic properties of this thin-film material deposited on a graphite substrate.

2. Experimental details
For preparation of WSe$_2$/WO$_3$ layers, pulsed laser deposition (PLD) of W-Se-O films was carried out, and then the deposited films were subjected to thermal post-treatment (annealing). An yttrium-aluminium-garnet laser (wavelength 1.06 µm) was used for PLD with a pulse duration of 15 ns, a repetition rate of 25 Hz, and a pulse energy of 30 mJ. The fluence in the laser spot was ~8 J/cm$^2$. The WSe$_2$ target for PLD was manufactured by means of cold compacting technology under the pressure of 600 MPa using WSe$_2$ powder obtained by self-propagating high-temperature synthesis.

A deposition chamber was evacuated to a pressure of ~10$^{-4}$ Pa. The deposition of the films was carried out in vacuum (residual gas pressure was ~10$^{-4}$ Pa) and at various pressures of buffer/reactive gases. Buffer argon (Ar), reactive oxygen (O$_2$), and mixture of Ar and O$_2$ gases was introduced into the chamber after evacuation. The W-Se-O films were deposited at room temperature on substrates made from polished graphite. The obtained W-Se-O films were annealed at 450 °C and 550 °C for 30 min in Ar at a pressure of 10$^3$ Pa.

Surface morphology of the substrate and deposited films, structure and chemical composition were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and micro-Raman spectroscopy (MRS, laser wavelengths were 488 and 647 nm). The catalytic activity of the prepared coatings on the graphite substrates was studied in 0.5M H$_2$SO$_4$ solution at room temperature with a typical three-electrode electrochemical cell setup. Potential was measured relative to the standard hydrogen electrode.

3. Results and discussions
Figure 1 shows surface morphology of the polished graphite substrate prior the film deposition. The pristine substrate consisted of randomly oriented graphite sheets having the sizes of several micrometers.

![Figure 1. SEM images with two magnifications for the](image)
polished graphite substrate.

Surface morphology and composition of the pre-deposited W-Se-O films strongly dependent on the pressure and composition of the used gas. The deposition in the residual gas resulted in the formation of W-enriched films (WSe$_{0.3}$) which possessed relatively smooth surface and contained ball-shaped nanoparticles (Figure 2a). These nanoparticles were made of β-W [9] and they were ejected from the WSe$_2$ target due to pulsed laser irradiation. Incorporation of oxygen from the residual gas into the bulk of the films was negligible.

![Figure 2. SEM images for W-Se-O films prepared by PLD in (a) vacuum conditions; (b) O$_2$ gas; (c) Ar+O$_2$ gas mixture at a pressure of 5 Pa; (d) Ar+O$_2$ mixture at a pressure of 20 Pa.](image)

The use of O$_2$ gas for PLD at a pressure of 7 Pa did not alter the morphology of the films but the oxygen addition was realized and WSe$_{0.5}$O$_2$ film was formed (Figure 2b). As a rule, the PLD of TMDs in a gas should result in a significant increase in the chalcogen atoms content for TMD films [10]. The increase of chalcogen atoms content is caused by the decrease of energy for condensed atoms with consequence, in particular, on preferential sputtering of chalcogen atoms. In fact, a large increase of Se/W ratio was detected for the W-Se-O films when the deposition was performed in Ar+O$_2$ gas mixture with relatively lower O$_2$ concentration (~10%). For such gas mixture composition at a pressure of 5 Pa, WSe$_2$O$_{0.8}$ film was prepared. The comparison of the films prepared in O$_2$ and Ar+O$_2$(10%) mixture shows that in the case of a high O$_2$ content in the gas, Se atoms could be removed from the W-Se-O film due to volatile selenium oxide formation and/or Se-O molecules formation in collisions of Se atoms with O$_2$ molecules. The WSe$_2$O$_{0.8}$ film consisted of round-shaped nanoparticles having 50 – 100 nm sizes (Figure 2c).

SEM and EDS studies of the films prepared by PLD at higher pressure of Ar+O$_2$(50%) gas mixture (the pressure was ~20 Pa) showed that the concentration of oxygen in the films has increased significantly and the porous/sponge-like WSeO$_3$ films were grown (Figure 2d). These films had nonuniform distribution and low adhesion on the substrate. Thermal post-treatment of the prepared films at a temperature of 450 °C caused insignificant modification of their surface morphology (Figure 3) and Se content has decreased to some extent.

![Figure 3. SEM images for various W-Se-O films after annealing at a temperature of 450 °C. SEM images of the pre-deposited W-Se-O films are shown in Figure 2 (a), (b), (c), and (d), respectively.](image)
Figure 4 shows MRS spectra measured for various W-Se-O films before and after annealing at 450 °C. Laser wavelength was 647 nm. MRS spectrum of the polished graphite substrate had two narrow G and D peaks at ~1580 cm\(^{-1}\) and ~1360 cm\(^{-1}\), respectively (results not presented). Deposition of the W-Se-O films caused the appearance of several broadened lines in the range of wave numbers from 200 cm\(^{-1}\) to 300 cm\(^{-1}\). The most intense line was near 252 cm\(^{-1}\). The position and shape of this line indicated the formation of a disordered structure, in which a short-range order as in 2H-WSe\(_2\) phase and/or pure Se phase could be arranged. After annealing at 450 °C, MRS spectra contained two broad bands, the first one at low frequency in the range 300–700 cm\(^{-1}\) and the second one at 800–1000 cm\(^{-1}\). Such spectra are characteristic of quasi-crystalline WO\(_3\) films [11].

![Figure 4](Image)

**Figure 4.** MRS spectra measured (a) before and (b) after annealing at 450 °C for W-Se-O films prepared by PLD in vacuum (1), O\(_2\) gas (2), (c) Ar+O\(_2\) gas mixture at a pressure of 5 Pa (3) and Ar+O\(_2\) mixture at a pressure of 20 Pa (4).

Annealing of the WSe\(_2\)O\(_0.8\) film at a higher temperature caused significant reconstruction of the film and a "flower-like" morphology was observed by SEM (Figure 5). "Buds" of the flowers consisted of petals with a sheet-like structure. Dimensions of the sheets did not exceed 200 nm, and thicknesses of the sheets were several nanometers.

![Figure 5](Image)

**Figure 5.** SEM images with two magnifications for W-Se-O film containing WSe\(_2\) and WO\(_3\) nanosheets.

For annealed samples, MRS studies (laser wavelength was 488 nm) showed that the intensity of the line for the WSe\(_2\) nanophase at 257 cm\(^{-1}\) increased and new lines at 727, 813, and 963 cm\(^{-1}\) had arisen (Figure 6). The new lines correspond to WO\(_3\) phase and the specific line at 963 cm\(^{-1}\) reveals the nanometer dimensions of WO\(_3\) phase because this line corresponds to W=O boundary bonds in the WO\(_3\) nanocrystals.
Measurements of the cathodic polarization curves showed that only post-treatment at 550 °C resulted in a significant increase in the HER activity for W-Se-O films. The cathodic current density increased up to 50 mA/cm$^2$ at a potential of 100 mV. For comparison, the current density for the graphite cathode was about 7 mA/cm$^2$. Tafel curves could be extrapolated as linear dependencies in a relatively short range of cathodic currents. For the graphite cathode covered with the WSe$_2$/WO$_3$ nanosheets layer and without it, the Tafel slopes were ~90 mV/dec and 340 mV/dec, respectively. It should be noted that cathodic pretreatment at -500 mV was carried out to activate the hydrogen production. An improvement of the catalytic properties of the WSe$_2$/WO$_3$ catalysts could be achieved by optimizing their chemical composition and varying the annealing conditions.

![MRS spectrum for WSe$_2$/WO$_3$ nanosheets](image)

**Figure 6.** MRS spectrum for WSe$_2$/WO$_3$ nanosheets containing films prepared on the graphite substrate.

4. Conclusion
PLD of W-Se-O films in Ar+O$_2$ gas mixture followed by thermal annealing at a quite high temperature resulted in the formation of efficient catalysts for HER. These thin-film coatings had perpendicularly oriented few-layered WSe$_2$ and WO$_3$ sheets that uniformly covered graphite microcrystals. The cathodic electrochemical treatment of the nanosheets containing structure could initiate phase transformation/restructuring under hydrogen interaction with the WSe$_2$ and WO$_3$ phases.

Acknowledgments
This work was supported by Russian Science Foundation (project No 14–22–00098).

References
[1] Pumera M, Sofer Z and Ambrosi A 2014 *J. Mater. Chem. A* 2 8981–8987
[2] Wu Z, Fang B, Bonakdarpour A, Sun A, Wilkinson D P and Wang D 2012 *Appl. Catal. B* 125 59–66
[3] Mao S, Wen Z, Ci S, Guo X, Ostrikov K and Chen J 2014 *Small* 11 414–419
[4] Vrubel H, Moehl T, Grätzel M and Hu X 2013 *Chem. Commun.* 49 8985–8987
[5] Tang H, Dou K, Kaun C-C, Kuang Q and Yang, S 2014 *J. Mater. Chem. A* 2 360–364
[6] Zhuiykov S and Kats E 2014 *Nanoscale Res. Lett.* 9 401
[7] Ketpang K, Kim M, Kim S and Shanmugam S 2013 *Inter. J. Hydrogen Energy* 38 9732–9740
[8] Fominski V Y, Grigoriev S N, Romanov R I, Zuev V V and Grigoriev V V 2012 *Semiconductors* 46 401–9
[9] Fominski V Yu, Grigoriev S N, Celis J P, Romanov R I and Oshurko V B 2012 *Thin Solid Films* 520 6467–6483
[10] Grigoriev S N, Fominski V Yu, Gnedovets A G and Romanov R I 2012 *Appl. Surf. Sci.* 258 7000–7007
[11] Filipescu M, Orlando S, Russo V, Lamperti A, Purice A, Moldovan A and Dinescu M 2007 *Appl. Surf. Sci.* 253 8258–8262