Selection of pulsed laser deposition conditions for preparation of perfect thin-film MoS\textsubscript{x} hydrogen evolution catalysts

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Abstract. The influence of pulsed laser deposition conditions in the geometry "off-axis" on the catalytic properties of MoS\textsubscript{x} films in the hydrogen evolution reaction is investigated. For the deposition of MoS\textsubscript{x} films from MoS\textsubscript{2} target, pulsed laser radiation from the IR and UV wavelength ranges was used. The angle of incidence of the laser-induced plume on the surface of the substrate in a buffer gas was varied to check the influence of large in-size Mo-enriched particles. The efficiency of the catalyst was estimated from the results of the turnover frequency (TOF) measurement, which made it possible to minimize the influence of the "loading" of the catalyst on its characteristics. The effects of the chemical composition, local structure, and properties of the catalyst–substrate interface on the efficiency of the hydrogen evolution reaction are analysed. The regime of pulsed laser deposition of more effective thin-film MoS\textsubscript{x} catalysts is determined.

1. Introduction

Recent studies have shown that thin-film forms of transition metal dichalcogenides (TMD), in particular molybdenum sulfide (MoS\textsubscript{2}), can exhibit high electrocatalytic activity in the hydrogen evolution reaction (HER) [1,2]. Catalytically active sites were found on the edges of ultrathin layered MoS\textsubscript{2} structures, on the defect areas of the basal planes of such films, as well as on certain atoms of amorphous modifications of MoS\textsubscript{2} [3,4]. Amorphous films of molybdenum sulfide attract interest because it is not necessary to solve the problem of forming clusters with a certain orientation to the substrate surface to obtain high density of catalytically active sites on the catalysts surface [5].

Pulsed laser deposition (PLD) allows to obtain effective TMD containing catalysts with different chemical and structural states, in which both amorphous regions and nanocrystalline inclusions can be present [6,7]. The realized structural state (local atomic packages) largely depends on the conditions for obtaining and depositing a laser plume. In the case of laser ablation of the target MoS\textsubscript{2} by laser pulses with a wavelength from the IR range (1.06 μm), relatively large particles enriched in molybdenum are inevitably formed [8]. In the case of the deposition of the plume along the normal to the surface of the substrate, these particles have an important influence on the morphology of the catalyst, since they increase the real area of its surface. In the case of the application of the deposition geometry by a sliding plume, large particles practically did not settle on the substrate [9].
The aim of the study was to investigate the influence of the conditions of laser plume generation and deposition on the catalytic activity of MoS$_x$ films, which were created under the geometry of the off-axis PLD onto a substrate of glassy carbon (GC). In the case of deposition of relatively large particles enriched in Mo, the chemical nature of the catalyst support can be changed, and two types of MoS$_x$/Mo and MoS$_x$/GC interfaces may be realized. It is important to separate the effects in the catalytic hydrogen evolution associated with 1) an increase in the surface area; 2) the formation of catalytically active sites of various nature, including the appearance of pure Mo on the surface and 3) the appearance of interfaces of MoS$_x$/Mo and MoS$_x$/GC.

2. Experimental methods

For ablation of the target MoS$_2$, nanosecond pulses with a wavelength of 1064 and 266 nm were used. For both wavelengths, the laser fluence of the target irradiation was chosen from the condition for the formation of a plasma plume with a low concentration of sparks which could be caused by the formation of large particles. The resulting laser plume propagated along the direction of the normal to the surface of the target in argon at a pressure of 5 Pa. GC substrates were located at some distance from the axis of the laser plume expansion (figure 1). Thus, the direction of movement of the plume fraction was chosen, in which the sulfur concentration could be quite high [10]. In this case, the substrates were installed at different angles ($\theta$) to the direction of propagation of the laser plume. This angle was varied in the interval $0^\circ$–$90^\circ$. Film deposition time at any conditions was 8 min. The PLD was made at room temperature of GC substrate.

![Figure 1. PLD of MoS$_x$ films with various configuration of the off-axis deposition from MoS$_2$ target.](image)

Structural and morphological characteristics of MoS$_x$ films were studied by scanning electron (SEM) and transmission electron microscopy and microdiffraction (TEM and MD) methods, supplemented with energy-dispersive X-ray spectroscopy (EDXS). To analyze the catalytic activity of films, a traditional set of methods for electrochemical measurements in 0.25 M H$_2$SO$_4$ was used. The turnover frequency (TOF) was chosen as the main criterion of comparison, which made it possible to reduce the dependence of the catalytic characteristics of the prepared MoS$_x$ films on the loading (thickness) of the catalytic material.

For estimation of TOF, a technique was used in which a cyclic voltammogram was measured in the range from -50 to +1150 mV after applying the cathodic polarization [11]. Integration of current peaks resulted from the oxidation of active sites allows estimating the number of active sites on the catalyst surface. The normalization of the current density, which is measured by linear voltammograms, by the number of catalytically active sites allows us to calculate the TOF of the catalyst.

3. Results and discussions

Figure 2 shows the characteristic morphology of MoS$_x$ films, which were obtained by the off-axis PLD method with a wavelength of 1064 and 266 nm on the GC substrates. The substrates were placed at different angles to the axis of expansion of the laser plume. It can be seen that the wavelength did not have a significant effect on the morphology of the film, which for $\theta=90^\circ$ contained a high surface
concentration of rounded particles of micron and submicron sizes. It was previously established that these particles are enriched in molybdenum [9].

![Figure 2. SEM images of MoS$_x$ films, which was prepared by off-axis PLD at various $\theta$: (a,b) $\theta=90^\circ$ and wavelength 1064 and 266 nm, respectively; (c) $\theta=0^\circ$ and wavelength 1064 nm; (d) $\theta=30^\circ$ and wavelength 1064 nm.](image)

When the substrate was turned parallel to the axis of expansion of the plume ($\theta=0^\circ$), the Mo particles were deposited in a much smaller amount, and the morphology of the film consisted of densely packed nanoparticles up to 50 nm in size. In the intermediate position (angle) of the substrate, the submicron-sized Mo particles are deposited onto the substrate, and the larger particles are deformed due to spreading over the GC surface. As a result, the height of such particles above the surface decreased noticeably (figure 2).

Measurements of the ratio $x=S/Mo$ by the EDXS method have shown that at normal incidence of the plume $x \leq 2$. A decrease of an angle of the substrate tilt caused a noticeable increase in the sulfur concentration ($x \geq 3$).

The results of TEM studies of prepared films are shown in figure 3. For MoS$_x$ films obtained at $90^\circ$, regions with relatively high-quality laminar packing of Mo and S atoms in a hexagonal 2H-MoS$_2$ lattice were observed (figure 3 (a)). The crystals sizes were no more than 15 nm, and the distances between the basal planes were $\sim 0.6$ nm. In addition to such local areas with an ordered structure, regions with amorphous atomic packing, which corresponded to diffuse reflections in the microdiffraction pattern, were also found for this film (results not presented). Films obtained at other angles of deposition of the laser plume had a more disordered structure [10]. However, high resolution TEM studies revealed the presence of nanoclusters with laminar packing of molecular planes in these films. The distance between the planes was about 0.6 nm (figure 3(b)).
Figure 3. High resolution TEM and MD patterns for the MoS\textsubscript{x} films prepared by off-axis PLD on the substrates at \(\theta = 90^\circ\) (a) и \(\theta = 0^\circ\) (b).

Figure 4 shows the results of electrochemical studies of the prepared catalytic MoS\textsubscript{x} films. The deposition conditions significantly influenced the results of all the test types carried out. For the sample located at \(90^\circ\), the most intense peaks of oxidation of the active sites were observed. The peaks could correspond to Mo (630/678 mV) and molybdenum sulfide (700 mV). Other samples had peaks of 600 and 850 mV, which could correspond to oxidation of amorphous Mo-3S clusters. The results of the TOF calculations for the prepared MoS\textsubscript{x} films are given in table 1. According to calculations, the largest values of TOF were found in samples unfolded at an angle of 30° to the direction of expansion of the laser plume. At the same time, this sample demonstrated larger value of resistance to current transport during catalysis.

Figure 4. Linear (a) and cyclic (b) voltammograms, as well as Nyquist plots (c) for MoS\textsubscript{x} films, which were deposited at different angles between the direction of the laser plume expansion and the substrate surface.

The deposition of a large number of molybdenum particles actually could change the chemical nature of the thin film MoS\textsubscript{x} catalyst support. The influence of the nature of the interface of MoS\textsubscript{x} film with such supports as glassy carbon and molybdenum on the catalytic activity of MoS\textsubscript{x} was studied by calculating the change in the Gibbs binding energy (\(\Delta G\)) during the formation of a hydrogen molecule. The calculations were performed within the framework of the density functional theory (DFT) using the software package for quantum-mechanical calculations Quantum ESPRESSO in the basis of plane waves. Figure 5 shows two models that have been analyzed. In one model, the MoS\textsubscript{3} chain of atoms was located above a single graphite plane that mimicked a local region of glassy carbon, for which a graphite-like short-range order of atomic packing is characteristic. In another model, the MoS\textsubscript{3} chain...
was located above the atomic plane of Mo. The reliability of the chain model of the MoS$_x$ amorphous phase was considered in detail by Hibble and Wood [12]. Calculations have shown that absolute values of $\Delta G$ for the selected models differ only a little and the real values are 0.29 eV and -0.31 eV for the MoS$_3$/Mo(110) and MoS$_3$/GC contact regions, respectively.

### Table 1. Important catalytic characteristics of the obtained MoS$_x$ films.

| Deposition angle | Overvoltage, mV ($J=10$ mA/cm$^2$) | Tafel slope (mV) | TOF (s$^{-1}$) |
|-----------------|-------------------------------------|-----------------|--------------|
| $\theta = 0^\circ$ | 184                                 | 42.3            | 0.090        |
| $\theta = 30^\circ$ | 175                                 | 43.9            | 0.130        |
| $\theta = 45^\circ$ | 168                                 | 39.0            | 0.043        |
| $\theta = 90^\circ$ | 162                                 | 46.6            | 0.015        |

**Figure 5.** Atomic configurations, which were used for analysis of HER on the MoS$_3$ catalysis film under the influence of MoS$_3$/GC (a) and MoS$_3$/Mo (b) interfaces (Mo – blue, C – black, S – yellow).

Thus, the modification of the chemical nature of the support (Mo instead of GC) could not have a significant effect on the catalytic properties of MoS$_x$ films. It should be noted that DFT calculations were carried out for the chain modification of molybdenum sulfide. In the real case, the MoS$_x$ film contained amorphous and nanocrystalline phases.

### 4. Conclusions

In the case of production of thin-film MoSx catalysts by the PLD method from the MoS$_2$ target, the wavelength of the laser radiation had no appreciable effect on the morphology of the film. When the laser plume was deposited along the normal to the substrate surface, the prepared films consisted of micro- and submicro-meter Mo particles and a nanostructured matrix. When the substrate was oriented along the direction of plume motion, the contribution of the Mo particles to the film morphology was changed, since the Mo particles spread over the surface ($\theta=30^\circ$) or do not adhere to the surface at all ($\theta=0^\circ$). Deposition of Mo particles could increase the catalytic activity of MoS$_x$ films by increasing the surface area and improving the current transport. However, a more important factor is the local packing in the MoS$_x$ film, which largely depended on the angle of incidence of the laser plume. The most perfect catalytic MoS$_x$ films were obtained when the substrate was slightly tilted ($\theta=30^\circ$) to the direction of plume expansion and a combination of propagated and scattered atomic flows was realized for film growth.

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