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Preparation and study of thin films of tungsten selenides for electrocatalytic hydrogen evolution

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Abstract

Thin films of tungsten selenides (WSe_x) were obtained by using a method of shadow-masked pulsed laser deposition. The deposition at room temperature of substrates caused the formation of Se-enriched amorphous films (Se/W~5) with pronounced surface roughness because of an effective nanoparticle growth. Heating or DC biasing the substrate during the deposition modified the film composition (Se/W~1.7 – 4) and resulted in the smoothing of the film surface. Annealing the films, deposited at room temperature, as well as heating the substrate during the deposition caused crystallization of the films. Catalytic activity of WSe_x thin films in hydrogen evolution reaction (HER) was studied in 0.5 M H_2SO_4 aqueous solution at room temperature. The structural state and the chemical composition of WSe_x films had an expressed impact on the catalytic activity. A significant improvement in HER activity was observed in the case of Se-enriched films deposition followed by annealing at 500ºC.

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1. Introduction

Recently, nanoparticles of transition metal dichalcogenides (TMD) have been identified as promising hydrogen

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evolution catalysts. Bulk TMD is a poor catalyst Jaegermann and Tributsch (1988). Nano-crystals of TMD, however, are more active Jaramillo eta al. (2007), Kong eta la. (2013), Pumera et al. (2014). To receive high-quality electrocatalysts, the TMD films should satisfy several requirements. In particular, the surface area and the number of catalytically active sites on the TMD surface should be increased, and the effective charge transport should be provided. Theoretical and experimental investigation results have indicated that the edge sites of the sandwich-type structure of TMD are catalytically active for hydrogen evolution reaction (HER) Karunadasa et al. (2012), Le eta al. (2014). The studies have shown that the exchange current density of TMD nanocrystals is proportional to the length of the edge sites but not to the basal areas in truncated hexagons. However, the increase in catalytic activity was also observed for amorphous TMD thin films Merki et al. (2011).

To produce thin TMD films, different methods are used. The single-layer and few-layer TMD can be successfully produced with mechanical and liquid-phase exfoliation Plechinger (2014). For preparation of thin nanostructured films, the chemical vapour deposition (CVD) is widely Refs. used Plechinger (2014), Wang et al. (2013). The CVD of TMD films requires the use of sufficiently volatile precursors. The synthesis and application of dangerous chemical agents unavoidably aggravate ecological problems. This work is aimed to investigate the adjustability of the structure, morphology, chemical composition and HER activity of the thin films of tungsten selenides (WSe_x), which were prepared using the notably environmentally friendly methods of physical vapour deposition such as the pulsed laser deposition (PLD). The use of buffer gas and installation of a mask between the laser target and the substrate permits a stronger effect on the important characteristics of the atomic flux, which can cause essential changes in the structure and chemical composition of the films obtained by the PLD Grigoriev et al. (2014).

2. Experimental details

Radiation of the Q-switched Nd: YAG laser was scanned over the target holder using an automatic device in a vacuum chamber. The target was made of pressed WSe_2 powder. The duration of the laser pulse was ~15 ns and the pulse energy was ~ 30 mJ. The laser fluence in the focus spot was ~8 J/cm^2. A mask in the form of a thin disk (0.8 cm in diameter) was established in the path of the laser plume from the target. The distance between the target and the mask was 2 cm, and the distance between the mask and the substrate was 3.5 cm. The target, mask and substrate were set parallel to one another and perpendicular to the direction of movement of the laser plume. The chamber was evacuated to a residual pressure below 10^{-4} Pa, and the buffer Ar gas was introduced into the chamber until the pressure reached 2 Pa. Polished Si and carbon plates were used as substrates for the film deposition. During the PLD, the substrates were held at room temperature or at 200ºC. After the PLD preparation at room temperature, the films were annealed in Ar at 500ºC. The deposition was performed on non-biased or negatively DC (–200V) biased substrates.

The deposition rate and chemical composition were measured using Rutherford backscattering spectroscopy of helium ions (RBS). The surface morphology of the films was analysed using scanning electron microscopy with secondary electrons (SEM). The surface topography and root mean square roughness (S_q) of the films that were deposited on the Si substrate were examined using the atomic force microscopy (AFM). The local structure of the films was investigated using the laser micro-Raman spectroscopy (MRS) on NTEGRA Spectra (diameter of laser beam ~0.2 μm, wavelength 473 nm). The HER catalytic activity of WSe_x films on carbon substrates was studied in 0.5 M H_2SO_4 solution at room temperature with a typical three-electrode electrochemical cell setup. The cathodic polarization curves were measured at a slow scan rate of 1.5 mV/s. The potential was measured in relation to the standard hydrogen electrode.

3. Results and discussions

3.1. Features of shadow-masked PLD used for WSe_x films preparation

Fig. 1a demonstrates the results of mathematical modeling of the flux of W and Se atoms deposited on the substrate during the PLD from the WSe_2 target in Ar gas at a pressure of 2 Pa. The laser plume movement in a buffer gas around the mask was simulated using the version of the direct simulation Monte Carlo method described by Bird (1994), which takes into consideration collisions of plume atoms with buffer gas atoms, while collisions