Regulation of nanoparticle impact on the growth of MoSe$_x$ films during pulsed laser evaporation of MoSe$_2$ target

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Abstract. Irradiation of MoSe$_2$ target with intensive laser pulses caused the formation of micro- and nanoparticles. The particles were observed on the target surface and in MoSe$_x$ films prepared by deposition of the laser-induced plume. Content of nanoparticles on the film surface was markedly larger than that of microparticles. Transport of the plume in vacuum and in a buffer helium (He) gas was studied. The He pressure was high enough to provide effective atom scattering and plume deceleration. For a medium target-substrate distance, the structure of MoSe$_x$ film was formed due to intensive deposition of atomic flux scattered in the buffer gas. Impact of nanoparticles on the structure was negligible. For a large distance, deposition of the nanoparticles from the plume was assisted by co-deposition of drifting atomic flux. Such deposition resulted in the formation of relatively smooth film containing nanoparticles transferred with plume, as well as the growth of spherical Se particles on the substrate.

1. Introduction

Sen et al. [1], Fominski et al. [2], and Hu et al. [3] have observed the nanoparticles formation during pulsed laser deposition (PLD) of transition metal dichalcogenides (TMDs, Mo/W/S$_x$/Se$_x$) films. Grigoriev et al. [4] revealed the important influence of Mo nanoparticles on the structure of the PLD MoSe$_x$ films and their catalytic properties in hydrogen evolution reaction. The possibility of a positive effect of nanoparticles on the tribological properties of gradient Mo-Se-Ni-C coatings obtained by PLD was proposed by Grigoriev et al. [5].

At present, an interest to study the mechanisms of nanoparticles formation under pulsed laser irradiation/ablation and the impact of nanoparticles on the structural and functional properties of thin films increases (e.g., Cao et al. [6]). The aim of this work was to investigate the formation of nanoparticles during pulsed laser irradiation of MoSe$_2$ target and the transport of these particles from the target to MoSe$_x$ films formed due to the deposition of the laser-induced plume. The transport and deposition of the laser plume were studied in vacuum and in a buffer gas with a relatively high pressure. Inert helium (He) was used as a buffer gas to change the dynamics of atomic particles of the
laser plume. The transport of the laser plume at the different conditions was monitored by measuring the time-of-flight signals for the pulsed laser plasma.

2. Experimental details

An electro-optically Q-switched yttrium-aluminium-garnet laser with wavelength of 1.06 µm and a pulse duration of 15 ns was used for PLD. For irradiation of MoSe$_2$ target, a relatively high laser fluence of ~8×10$^8$ W/cm$^2$ was used. The deposition chamber was evacuated to a pressure of ~10$^{-4}$ Pa. Hereinafter, PLD at a pressure of ~10$^{-4}$ Pa will be referred to as PLD in vacuum. In some experiments, the buffer He gas with pressure of 30 Pa was introduced into the chamber after evacuation. This option will be denoted as PLD in He gas. The laser plume was directed along the normal toward the substrate surface. Si substrates were placed at 5 or 10 cm from the target.

To control the transport of ionized laser plume in various conditions, time-of-flight ion signals were detected in places of the target location. Surface morphology of the target and the deposited films was characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and micro-Raman spectroscopy (MRS).

The MoSe$_2$ target for PLD was manufactured by means of cold compacting technology under the pressure of 600 MPa using MoSe$_2$ powder obtained by self-propagating high-temperature synthesis. The MoSe$_2$ powder was synthesized from Mo powder of 99.93% purity and particle size of 1–4 µm, and Se powder of 99.997% purity. The pressed target was composed of MoSe$_2$ microcrystals having a lamellar shape. EDS measurements showed that the elements (Mo and Se) were fairly uniformly distributed throughout the volume of the microcrystals. Chemical composition of the synthesized microcrystals was equal to a stoichiometric value. Prior to pulsed laser irradiation, the surface of the pressed MoSe$_2$ target was treated mechanically (grinding, polishing) and washed with the alcohol.

3. Results and discussion

Figure 1 shows SEM images of the surface of a polished MoSe$_2$ target before and after pulsed laser irradiation under vacuum conditions. Mechanical treatment of the target removed the microcrystalline morphology/roughness and caused the enrichment of the surface layer with Se. Mean value of ratio $x = \text{Se/Mo}$ was ~10. Pulsed laser irradiation caused melting of the surface and Se content ($x \sim 1.7$) in the surface layer decreased. Mo- and Se-enriched nano- and micro-particles were observed on the surface. The possible mechanisms of such particle formation were discussed in [2,4]. On the next step of pulsed irradiation, these particles could be captured by vapor flux and transferred from the target to MoSe$_2$ film.

Figure 1. SEM images of the surfaces: (a) polished MoSe$_2$ target; (b) and (c) the same target after pulsed laser irradiation.

Figure 2 shows ion signals measured at distances 5 and 10 cm for pulsed laser plasma initiated in vacuum and in He gas at 30 Pa. For a distance of 5 cm, presence of buffer He gas leads to a decrease of ion pulse intensity but a large fraction of the ion beam effectively penetrates trough the gas.
Calculations with models of Fominski et al. [7] show that the atomic fraction of the plume can reach the substrate, but the energy of atoms is relatively low and atoms fall on the surface at various angles. For a distance of 10 cm and a pressure of 30 Pa, only very small fraction of ions penetrated through the gas and conserved their energy (Figure 2(b)). Main portion of the ion beam has arrived to the detector in “a long tail” of the ion pulse. In this case, the film is assumed to grow due to the deposition of the flow of drifting atoms and ions. Drift velocity of deposited atoms is caused by a movement of shock wave that arises in the He gas at a pressure of 30 Pa.

![Figure 2](image)

**Figure 2.** Ion signals of pulsed laser plasma measured in (1) vacuum and (2) He at 30 Pa for two distances from the target: (a) 5 cm; (b) 10 cm.

Results of SEM studies of the MoSe$_x$ films prepared by PLD at various conditions are shown in Figures 3 and 4. For PLD at a distance of 5 cm (Figure 3), the vacuum deposited film consisted of dense matrix that contained spherical nanoparticles. The mean value of ratio $x$ was 1.2. The main content of the particles had the size in a range ~5 – 50 nm and the ratio $x$ for particles varied in a range ~0.8 – 2.5. For PLD in He, the film thickness and the Se concentration were larger than that for the vacuum deposited film. This film had a granulated morphology and the average size of the granules was ~50 nm. The growth of the granulates was probably initiated by scattered atomic flux deposition on the surface of smaller nanoparticles. When $x$ exceeds 3 in the MoSe$_x$ film, the deposition of excess selenium could make contribution to processes of the granules formation.

![Figure 3](image)

**Figure 3.** SEM images of the surface of MoSe$_x$ films deposited at a distance of 5 cm in (a) vacuum and (b) He gas at 30 Pa.

Transport of nanoparticles ejected from the target surface or formed in the laser plume is described by a drag model which is given by $X(t) = L_p[1 - \exp(-t/\tau_p)]$, where $L_p = v_0\tau_p$ is the nanoparticle...
stopping distance, \( v_0 \) is the initial nanoparticle velocity, and \( \tau_p \) is the relaxation time. In the free-molecular regime (e.g., Smirnov [8]), the relaxation time is \( \tau_p = (3/8)(M_p/R_p^2 P)(kT/2\pi m)^{1/2} \), where \( k \) is Boltzmann constant; \( R_p \) and \( M_p \) are the nanoparticle radius and mass; \( m, T \) and \( P \) are the molecule mass, temperature and pressure of the ambient gas, respectively. For 10 nm sized nanoparticles of Mo and Se in He gas at a pressure of 30 Pa, estimates give the values of the relaxation time \( \tau_p \sim 8.5 \times 10^{-4} \) s and \( 4.0 \times 10^{-4} \) s, respectively. Thus, nanoparticles having this size and larger with the initial velocity in the range \( \sim 0.1 \) – \( 1 \) km/s could effectively penetrate through the gas and bombard the substrate located at a distance of \( 5 \) – \( 10 \) cm from the target.

For PLD in vacuum at a distance of 10 cm, the deposited film possessed the specific surface morphology modulated at the nanoscale. Figure 4 (a) shows that the sizes of “nanoparticles” were distributed mainly in the range \( 5 \) – \( 50 \) nm. The film deposited in He gas was relatively smooth. The content of “nanoparticles” with the sizes \( 5 \) – \( 50 \) nm was not so large, but the content of spherical nanoparticles with the sizes \( 50 \) – \( 100 \) nm has increased essentially. According to EDS measurements, these larger particles were enriched with Se. The formation of nanostructure of the vacuum-deposited film was probably induced by self-sputtering of the film by energetic atoms (neutrals and ions). The Mo-enriched nanoparticles were not sputtered so effectively as the film matrix and the inclusions of Mo-enriched nanoparticles caused the corrugate surface formation. Figure 5 (a) shows SEM images (side view) of the MoSe\(_x\) film illustrating nanostructure character of this film.

![Figure 4](image_url)

**Figure 4.** SEM images of the surface of MoSe\(_x\) films deposited at a distance of 10 cm in (a) vacuum and (b) He gas at a pressure of 30 Pa. Inserts show the particle lateral size distributions measured on an area of \( 5 \times 5 \) \( \mu \)m\(^2\).

![Figure 5](image_url)

**Figure 5.** Cross-section SEM images of the MoSe\(_x\) films deposited on Si substrate at a distance of 10 cm in (a) vacuum and (b) He gas at a pressure of 30 Pa.

For PLD in He gas at a distance of 10 cm, the buffer gas prevents an intensive bombardment of the film with energetic atoms. Figures 4 (b) and 5 (b) show that in the case of drifted atoms deposition, the smooth matrix could be grown and the small Mo-enriched nanoparticles would be captured in it. In such conditions, the particles do not essentially influence on the film morphology. The EDS measurement has shown that the ratio \( x \) was \( \sim 2 \). Selenium was concentrated in isolated spherical Se
nanoparticles and the MoSe$_x$ film was enriched with molybdenum. MRS studies have shown (results not presented) that selenium condensation resulted in appearance of intense line at 234 cm$^{-1}$ in the Raman spectrum corresponding to nanocrystalline Se phase.

4. Conclusions
In this work, the formation of nano- and micro-particles on the surface of the laser-irradiated MoSe$_2$ target was observed. The particles had various composition and they were enriched with Mo or Se. For the condition of PLD used in this work, the transfer of particles from the target to the substrate was assisted with vapor flux transport and co-deposition that occurred on the substrate. The formation of the composition and morphology of the MoSe$_x$ films deposited on the substrate strongly depends on the dynamic characteristics of the vapor flux.

For PLD in vacuum, the bombardment of the growing films with high energy atoms induced sputtering of Se-enriched phase and the consequent nanostructuring of the film was developed. The buffer He gas has changed the dynamic of the laser plume but it could not prevent the deposition of the vapor flux even at a high pressure and a large distance from the target. For PLD at a medium target-substrate distance, the deposition of the scattered vapor flux causes granulated morphology formation. For PLD at a large distance, the Se vapor condenses on the substrate and larger Se particles are formed. The deposited Mo nanoparticles are captured in the bulk of the grown film due to the deposition of drifted vapor flux.

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