



# Structure and mechanical properties of W–Se–C/diamond-like carbon and W–Se/diamond-like carbon bi-layer coatings prepared by pulsed laser deposition

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## ABSTRACT

Bi-layer W–Se–C/diamond-like carbon (DLC) and WSe<sub>x</sub>/DLC coatings were obtained by standard and shadow-masked pulsed laser co-deposition from WSe<sub>2</sub> and graphite targets. W–Se–C coatings appeared as nanocomposites containing quasi-amorphous WSe<sub>2</sub>, WC, spherical β-W nanocrystalline particles encapsulated in WSe<sub>2</sub> amorphous shell, and amorphous carbon phases. In WSe<sub>x</sub>/DLC coatings, the formation of chemical bonds between W and C atoms was noticed at the interface. An increase of the C concentration over 40 at.% increases hardness and elasticity (up to 2 times at ~60 at.%C), and the Se/W ratio was always close to 1.4. The use of shadow-masked configuration avoids the deposition of micro- and nanoparticles. However, this method leads to a substantial increase of the Se content (Se/W ≥ 4), and the coatings became softer.

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## 1. Introduction

Transition metal dichalcogenide (TMD) coatings such as MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub> are known to exhibit a low coefficient of friction in vacuum, dry air or noble gas atmospheres. However, in the presence of oxygen and water vapor in the atmosphere or high temperatures, pure TMD coatings exhibit limited lubrication properties and a reduced wear resistance. Some other drawbacks are that the chemically inert TMD compounds have a poor adhesion to the substrate, and have a low hardness what results in a low load-bearing capacity.

One of the possible ways to overcome these difficulties is to alloy TMD coatings with various metals or nitrogen or by a combination of metal and nitrogen [1–5]. The doping of TMD coatings with carbon is also a promising way to improve their tribological properties. Carbon containing TMD coatings were extensively studied during the past decade [6–12]. It was found that after carbon doping the coatings became more dense, lost their columnar structure, and that the coating hardness increased linearly with increasing carbon content. The resulting structure of the coatings strongly depends on the chemical content of TMD material. W–S–C coatings can be described as nanocomposites

containing WS<sub>2</sub>, WC and diamond-like carbon (DLC) phases [6], while the Mo–Se–C was nanostructured coating contain MoSe<sub>2</sub> grains embedded into a carbon matrix [8]. The coatings exhibited an extremely low coefficient of friction (~0.05) at elevated temperature and a low wear rate [8,9]. In general, the tribological behavior of W–Se–C coatings is very close to that of other TMD + C systems, such as W–S–C and Mo–Se–C [12]. It was also found that the deposition of Mo–S–C coatings together with a co-sputtering of a MoS<sub>2</sub> and carbon target could lead to a layered structure formation. When thickness of coating nanolayers was lower, better tribological properties of the coating have been obtained [7].

Most of the TMD-based coatings studies are related to layers obtained by ion-sputtering techniques. The pulsed laser deposition (PLD) is not as common as ion-sputtering. However during PLD, the energy of atoms or ions in the laser plasma can be about hundreds of electron-volts while the concentration of high-energy particles in a laser-induced plume can exceed 10%. The properties of TMD-based coatings depend on the laser-induced plume characteristics and hence can be controlled by varying the laser irradiation parameters [13–17]. Pulsed laser deposition is a well known method for producing high-quality diamond-like carbon coatings also. That deals with the presence of high-energy atoms in laser plasma which is a necessary condition for the formation of sp<sup>3</sup> chemical bonds between carbon atoms [18].

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Another important feature of pulsed laser deposition of TMD is the formation of metal nanoparticles [13,15,19]. High-resolution transmission electron microscopy [19] has proved that these particles contain metal nuclei and laminar TMD shells. The mechanism behind this particle formation as well as the dependence of their properties on experimental conditions, are still unknown. The role of these nanoparticles on the mechanical properties of TMD-based coatings is not yet clear.

One of the most important disadvantages of the synthesis by PLD of TMD-based coatings is the deposition of micron and submicron-sized particles [15–17]. In presence of these particles, the growth of multilayered structures with sharp boundaries between nm-sized sublayers, is almost impossible [20]. Methods exist to eliminate such particles from films produced by PLD [21,22]. A shadow mask can e.g. be inserted between the target and the substrate. As a result, the micro-particles are mainly scattered and stopped by the mask, undergo backstreaming or deposition, while the atoms turn around the mask into the substrate-mask zone. Shadow-masked PLD offers the possibility to prepare particles-free coatings when the substrate is placed in the shadow region. However, the use of shadow-masked PLD for TMD-based coatings preparation has not yet been studied.

The purpose of this research was to study the structure, the chemical content and mechanical properties of thin  $WSe_x$ -based ( $W$ - $Se$ - $C$  and  $WSe_x$ ) films on hard DLC layer by pulsed laser deposition under vacuum conditions and by shadow-masked PLD in a buffer gas ( $Ar$ ). A buffer gas can have an essential impact on the propagation of a laser plume from  $WSe_2$  target to the substrate and on the chemical composition of  $WSe_x$  films at usual PLD [23]. But preliminary experiments showed that the application of a shadow-masked configuration of PLD under vacuum conditions completely suppresses the deposition of atoms in the shadow area, and a buffer gas is necessarily to raise the efficiency of the transport of atoms from a laser target to a shadow area.

## 2. Experimental details

Bi-layer coatings were obtained by depositing in a first step a thin DLC film on a substrate by pulse laser deposition from a graphite target. In a second step,  $W$ - $Se$ - $C$  or  $W$ - $Se$  coatings were deposited on top of the DLC layer. The angle between the laser beam and the target surface was  $45^\circ$ . The substrate was placed parallel to the target surface thus perpendicular to the particle flow. The distance between target and substrate was 5 cm in all cases.

$NaCl$  and silicon mono-crystals as well as polished steel disks (steel 95Cr18) were used as substrates. The film thickness was varied accordingly to requirements of the different analytic methods used. Laser pulses with wavelength 1064 nm, pulse energy  $\sim 50$  mJ, and a repetition rate of 25 Hz, have been directed onto a target consisting of two plates. The first plate was made of graphite. The second plate was made of microcrystalline  $WSe_2$  obtained from pressed  $WSe_2$  powder. Details on the  $WSe_2$  target fabrication procedure can be found in [15]. The energy density of laser irradiation was about  $\sim 20$  J/cm<sup>2</sup>. The residual gas pressure in the vacuum chamber did not exceed  $5 \times 10^{-4}$  Pa during deposition. The scanning of the mosaic target surface under the laser beam was controlled automatically so that the deposition per scan would not exceed one monolayer. The carbon concentration in the resulting film was controlled by changing the duration of the irradiation of the graphite target.

Shadow-masked PLD was achieved by shielding with a disk (diameter 8 mm) mounted between  $WSe_2$  target and substrate. The distance between the target and mask was 2 cm. The laser plume ejected from the graphite target propagated freely from the target to the substrate by-passing the mask. The deposition chamber was filled with  $Ar$  gas at a pressure of about 2 Pa. Droplets and particles produced during the laser irradiation of the  $WSe_2$  target expanded mostly along straight trajectories, and were deposited on the mask. A flow of atoms that scattered at fairly large angles in collisions

with vapor atoms of the ablation plume and with inert gas molecules, propagated beyond the mask. All the films studied in this work were obtained in the center of the shadow zone. The center of the deposition zone coincided with the point where the perpendicular line drawn from the center of the laser irradiation zone on the  $WSe_2$  target meets the substrate surface.

Thus, in the case of PLD under vacuum conditions the substrate is bombarded by high velocity atoms and ions from two targets, namely  $WSe_2$  and graphite. In the case of shadow-masked PLD the substrate is bombarded by high velocity atoms and ions originated only from the graphite target. Additional research (results not shown) allowed to assume that the buffer gas ( $argon$ ) at a pressure of 2 Pa didn't have an appreciable impact on the transport of carbon ions from the graphite target to the substrate.

Helium ion Rutherford backscattering spectroscopy (RBS, ion energy 2 MeV, scattering angle  $170^\circ$ ) was used to analyze both thickness and chemical content of  $WSe_x$ -based films deposited on different substrates. In order to determine the thickness of the layers by RBS, the densities of  $WSe_x$ -based films have to be measured previously. Hereto, thin films of the corresponding materials were deposited on polished silicon surfaces. It offers the possibility to determine exactly the layer thickness (in "gram/cm<sup>2</sup>" units) by RBS measurements. The thickness of the layers was measured by comparing the height of the masked substrate area to the relative height of the coating surface with a contact profilometer.

Scanning electron microscopy (SEM, Cambridge Stereoscan S-360, accelerating voltage 20 kV) was used to investigate the topography of bi-layer coatings deposited on steel substrates. The surface morphology of the films deposited on Si substrate and the root mean square roughness,  $S_q$ , measurements were carried out with a scanning force microscope (SFM, Solver Pro-M, NT-MDT, Russia) in the contact mode using Si-tips NSG10 (tip radius 10 nm), NT-MDT. High resolution transmission electron microscopy and micro-diffraction (TEM and MD) done in an electron microscope JEM-2000EX (Jeol, Japan, the operating voltage 200 kV) were used to study the structure of films deposited on  $NaCl$  and Si substrates. Films deposited on  $NaCl$  substrates were placed on metal grids immersed in water, and then used for the electron microscopic investigation. The coatings deposited on Si substrate were investigated by cross-sectional TEM/MD. Samples for cross-sectional TEM observation were glued together with the coating surfaces facing each other using an adhesive and clamped till the epoxy was cured. The cured samples were ground mechanically to a foil with a thickness of about 30  $\mu m$ . This foil was further thinned down to electron transparency by ion polishing with a 4.5 keV  $Ar^+$  beam. In order to avoid analytical errors in the TEM/MD method, the DLC film thickness was kept as small as possible.

X-ray diffraction (XRD) and micro-Raman spectroscopy (MRS, Jobin Yvon-1000, wavelength 448 nm) were used to analyze the structure of bi-layer coatings deposited on steel substrate. In order to minimize the substrate effect, the X-ray diffractometer (Siemens, KRISTALLOFLEX-810) was operated at 30 kV and 20 mA in grazing incidence XRD mode using a 2-degree incident angle of monochromatic  $Cu K_\alpha$  radiation.

X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical state of the  $WSe_x$ -based coatings on Si substrate. XPS studies were also performed on  $WSe_2$  target. The XPS measurements were carried out with an XSAM 800 Kratos spectrometer using  $Mg K_\alpha$  radiation (photon energy 1253.6 eV). To prevent charging, thin Au films of about 2 nm thickness were deposited on the surfaces of all samples by thermal evaporation, and the binding energy of Au ( $Au 4f_{7/2}$ , 83.8 eV) was used as the charge-up correction. The chemical bonding at the interface of bi-layer  $WSe_x$ /DLC coatings was studied by recording successive XPS spectra obtained after ion etching for short periods. An  $Ar^+$  beam with 3-keV energy and a current density of 10  $\mu A/cm^2$  was used for sputtering. Relative XPS peak areas were used for quantifying the composition, and corrected for a spectrometer factor and X-ray cross-section.

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