

## CHALCOGENIDE-BASED AMORPHOUS THIN FILMS PREPARED BY PULSED LASER DEPOSITION

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General principles, advantages and drawbacks of pulsed laser deposition (PLD) technique for thin films preparation are briefly reviewed. The method is based on vacuum evaporation of material by intensive laser pulses and subsequent deposition of vapours on a substrate. The method is very promising for thin films preparation of complex composition materials. The deposition in non-inert (reactive) atmosphere is possible. Low volatility and refractory materials can be also deposited without decomposition. The application of PLD method for chalcogenide-based amorphous thin films preparation is also described and current state-of-the-art is reviewed. In the last time, the chalcogenide based waveguides, photoinduced effects, rare-earth doped chalcogenide films and different chalcogenide based sensors of complex composition have been prepared by PLD and studied most frequently.

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### 1. Introduction

Amorphous thin films based on chalcogens and chalcogenides of Ge, As, and on other elements are widely applied in optics, electronics, and optoelectronics (optical memories, gratings, waveguides, fibre and planar optical devices, optical sensors, optical circuits, holography, light amplifiers and generators, ionic sensors, etc. [1-15]). Amorphous chalcogenides form an important class of high-tech materials transparent in infrared region of spectra and applicable in chemistry, biology, medicine, ecology, optics, electronics, opto-electronics and material science and engineering. The unique optical properties (low phonon energies, intensive luminescence in NIR and MID infrared region, high linear and non-linear index of refraction and also photosensitivity of some of them) make them very interesting for integrated optical devices.

The preparation of amorphous chalcogenide thin films of large size, desired stoichiometry, sufficient homogeneity, good adhesion to the substrate, and other physico-chemical properties necessary for different applications is, however, a difficult task and classical deposition methods cannot be often used. Study of novel deposition techniques and methods for preparation of amorphous chalcogenide thin films is, therefore, of large interest and importance.

One of such relatively new deposition processes is the pulsed laser deposition (PLD) technique, known also as laser ablation. For evaporation of solid-state materials, the PLD process uses either high energy, short-wavelengths (UV) pulses from gas-based excimer laser systems (see, e.g. [1, 2, 5-7, 11, 13, 14, 16-50]) or intensive IR, visible or UV light pulses from solid state lasers (e.g. YAG: Nd<sup>3+</sup> laser, which produces pulses at 1064, 532, 355 or 266 nm, or Al<sub>2</sub>O<sub>3</sub>: Ti laser). The CO<sub>2</sub> continuous-wave laser light or the light of other powerful continuous lasers can be also applied for laser ablation, but the process is not of pulsed nature.

When the radiation from an intense pulse of ultraviolet excimer laser; namely of F<sub>2</sub>\* – 157 nm (7.89 eV); ArF\* – 193 nm (6.64 eV); KrF\* – 248 nm (5 eV); XeCl\* – 308 nm (4.02 eV);

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XeF<sup>\*</sup> – 351 nm (3.53 eV) or from other suitable pulsed laser system is absorbed by surface of solid-state material, the energy of photons is converted into thermal, and also chemical, electronic, and even in mechanical energy of particles, fragments, atoms or ions that are formed. It causes the evaporation, excitation and plasma formation (Fig. 1). The light does not only increase the surface temperature. The energy of laser pulses (for excimer lasers from ca. 3.5 to 7 eV, which corresponds to energies from 337.4 kJ/mol to 674.8 kJ/mol) can be higher than the energies of individual chemical bonds practically in any material (see, e.g. Table 1). The chemical bonds on the surface of target material can be then broken by high-energy photons, material is atomised and evaporated independently on volatility (partial vapour pressure) of its parts and fragments. High energy pulses allow evaporation and atomisation of chalcogenide-based glasses, but also of almost of any condensed material, e.g. metals [16, 51, 52], carbon [53], diamond [54], carbides [55], silicides [56], oxides [7,11, 57, 58], PbTe [18-20, 28], HgCdTe [31], CdS [29], CuInSe<sub>2</sub> [30], superconductors [59], hard nitrides [60], ferroelectrics [61], etc.

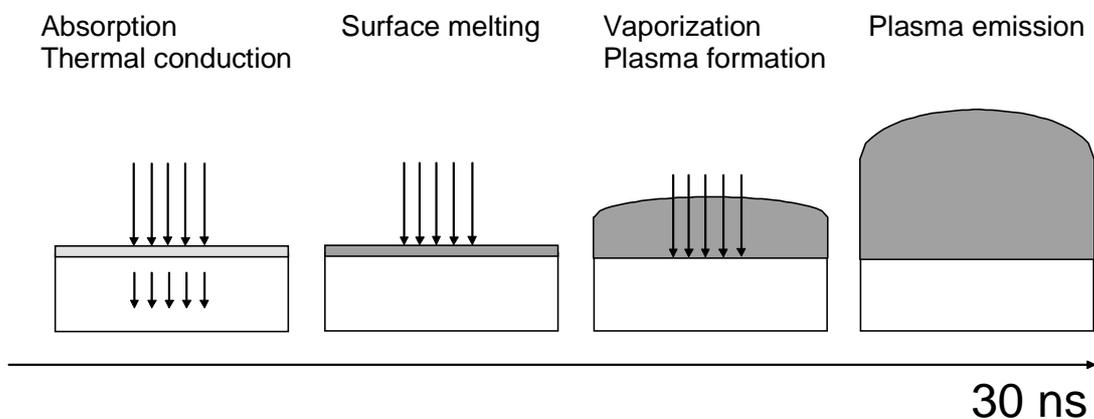


Fig. 1. Simplified scheme of the interaction between 30 ns laser pulse and solid-state target surface.

Table 1. Bond energies E (kJ/mol) for various atom pairs [69, 75-77]

Bond	E	Bond	E	Bond	E	Bond	E
S-S	280	P-Se	240	Sb-Te	195	Si-O	466
Se-Se	225	As-As	200	Si-Si	225	C-C	347
Se-Te	195	As-S	260	Si-Te	220	C-Si	301
S-Se	255	As-Se	230	Ge-Ge	185	H-H	436
Se-Te	220	As-Te	205	Ge-S	265	N-N	388
P-P	225	Sb-Sb	175	Ge-Se	230		
P-S	270	Sb-S	230	Ge-Te	200		

The mechanism of target evaporation is a complex process, which includes collisions, exfoliation, thermal, electronic, hydrodynamic, and condensational processes and phase explosion as primary mechanisms, and also different secondary mechanisms [19, 62]. The evaporated particles form a plume that contains energetic species such as atoms, molecules as well as electrons and ions, because the energy of the light in a pulse is so high, that also ions and electrons are produced [16]. The plume can contain also atomic and molecular clusters, molten globules and micron-sized solid particulates. Some authors suppose (see [63] and papers cited in) that the ablation by nanosecond pulses (at least of metals) causes only surface evaporation. So-called phase explosion – homogeneous nucleation of bubbles and their growth in highly superheated liquid proceeds at higher fluencies

( $\sim 7\text{-}30\text{ J/cm}^2$ ), at temperature above  $T/T_c \cong 0.8$ ,  $T_c \cong 10700\text{ K}$ ; the temperature of plasma is approximately  $8000\text{ K}$  [63].

The created plume can further absorb the energy of laser pulses, which penetrates the plasma, and is strongly absorbed. Due to this absorption, the temperature of the plasma increases and the plume is further ionised. Such absorption of energy in a plume is important mainly for high repetition rates of individual pulses exceeding  $500\text{ kHz}$ , because the plasma and neutral components of the plume need approximately  $1\text{-}10\text{ }\mu\text{s}$  to traverse the typical distance from target to substrate [64]. If necessary, in order to lower the absorption of light pulse with the plume, incident angle of the light can be lower than  $90^\circ$  (e.g.  $45^\circ$ , Fig. 2).

For thin films preparation is important that each laser pulse completely ablates a thin surface layer independently on vapour pressures of individual components of the target. The formed vapours and plume particles are subsequently deposited on appropriate substrate, the transfer of material from the target to substrate could be stoichiometric [1].

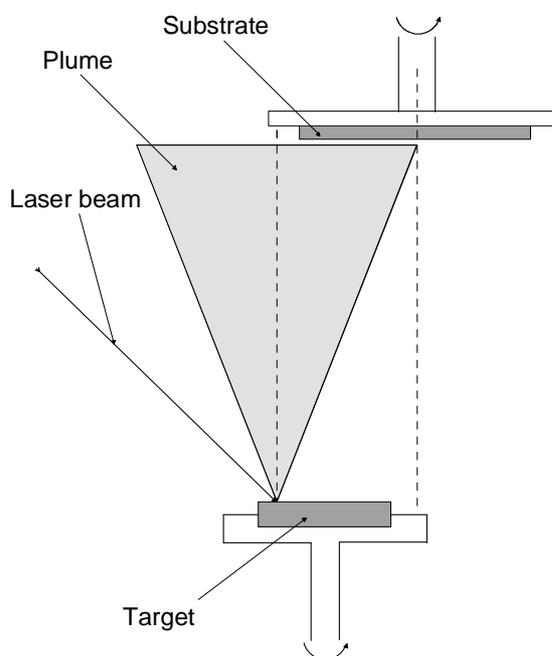


Fig. 2. Scheme of the off-axis PLD technique.

The temperature of the surface of target material can be very high. It was evaluated [20], that the surface temperature of many metals and oxides during PLD should be higher than  $3000\text{ K}$  (for vaporization rate of  $1\text{ nm/pulse}$ ), and for evaporation of tungsten, W, even  $T > 6000\text{ K}$ . Chalcogenides are generally more volatile; the temperature of their surface should be much lower. In some cases (lower fluencies and low repetition rates), the surface temperature should not be so high because the average energy delivered, is usually low (several  $\text{J/cm}^2$ ). Only the energy absorbed (and the effective temperature) during the short pulse duration is high. The evaluation of the temperature of the surface is generally very difficult problem and the error could be large (see, e.g. [18] and papers cited in). The process is a complex one, thermal models of evaporation by laser pulses are reviewed in [62].

Due to high temperature and high energy of light pulses, the unusual oxidation states of ions can occur in formed plasma plume. Above the target of Cu ( $308\text{ nm}$  excimer laser,  $3\text{-}7\text{ J/cm}^2$ ) were e.g. besides the  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions found also  $\text{Cu}^{5+}$ ,  $\text{Cu}^{4+}$ , and  $\text{Cu}^{3+}$  ions. It is interesting, that only  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions were formed by UV radiation ( $308\text{ nm}$ ), while also the  $\text{Cu}^{3+}$ ,  $\text{Cu}^{4+}$ , and  $\text{Cu}^{5+}$  ions were formed by intensive IR radiation pulses ( $1064\text{ nm}$ ) [16].

The PLD process can be controlled by adjustment of laser and deposition operating parameters (laser wavelength and power density, laser spot size on target, duration of light pulses, frequency of repetition of pulses, background pressure, background gas, etc.). The energy of a pulse as large as  $2 \times 10^{16}$  W/cm<sup>2</sup> was used for ablation [45] when intensive, focused, short (femtoseconds, fs) pulses were applied. Usually the energies are lower, of the order  $10^8$  W/cm<sup>2</sup>. Even in such a case, it is possible to evaporate volatile chalcogenides (e.g. As<sub>2</sub>S<sub>3</sub>) together with less- or non-volatile components and dopants at the same time, e.g. rare-earth and/or transition metals and/or compounds, alkali halides etc. [1, 2, 7, 13, 37, 39, 44, 49]. Usually the pulses of nanosecond duration are used. Recently, also very short high-power femtosecond pulses have been applied ([45, 54, 64] for example). The kinetic energy of ejected particles can be increased up to keV level and the velocity of emitted species can be of the order  $10^4$ - $10^5$  m/s [54]. Both, kinetic energy and velocity of particles, have a large influence on the quality of prepared films.

The parameters of light pulses and parameters of target material (conductivity, size, form, thickness, surface state) control the temperature, and also the ablation yields. For Cu ablation with 308 nm light pulses were e.g. obtained higher ablation yields at lower laser fluencies (3-10 J/cm<sup>2</sup>), but lower at higher fluencies (>10 J/cm<sup>2</sup>), when compared with YAG:Nd laser pulses (1064 nm) [16].

In case of chalcogenide-based materials, application of classical thin films deposition techniques (vacuum thermal evaporation, ion and magnetron or ionic sputtering etc.) leads often, due to different volatility of components or fragments of starting material, to non-homogeneous thin films of composition different from the target [13]. To compensate it, targets of composition different from the desired film stoichiometry should be then used. To find a proper composition of the target for a given case is a troublesome and difficult work.

In contrast with classical deposition techniques, the PLD of thin films of chalcogenides is a process, which can be often considered as stoichiometric one. In addition, the PLD can be relatively quick technique (temperature of the target surface is high) and chalcogenide films of thickness ~1000 nm or more can be prepared in few minutes depending on chemical composition of target material and other parameters of target and laser pulses [6]. It should be noted, that very quick ablation rates can lead to formation of particulates of materials caused by surface or subsurface boiling, and expulsion of the liquid, by plume shock wave pressure, and to some extent, by defoliation of target material [18]. Such splashing is considered as a drawback of PLD method and occurs in most materials except those with high vapour pressure below their melting points and targets with high thermal conductivity. The splashing is lower when lower energy pulses are used.

The films prepared by PLD technique possess sharp step of index of refraction between the substrate and the film [1] and higher density of deposited films due to higher kinetic energy of vapour particles. As mentioned above, the method is flexible in material use and has large variability in geometrical arrangements (e. g. inner surfaces films of hollow cylinders of high-temperature superconductors can be prepared) because the used pulsed laser system is external to the vacuum deposition chamber and light can be delivered to the holes and hollow structures etc. [47].

The properties (adhesion, morphology) of some films prepared by PLD technique can be further improved by so-called ion (plasma) – assisted pulsed laser deposition [20, 39]. As already mentioned, also electrons and ions are formed in a plume during excitation. They form an electrically conductive plasma in which a discharge can be initiated if DC bias voltage (positive or negative) is applied between substrate and ring-shaped electrode placed between substrate and target [20, 39]. This technique is capable of preventing or lowering the contamination of deposited films by ejected particulates. The particulates can be evaporated in the plasma; its temperature is further increased by the discharge. The discharge can improve also the stoichiometry, morphology and optical properties of the films [39]. Multiple thin films layers can be also prepared by PLD, e. g. by using multiple targets [65].

The PLD technique presents, however, several drawbacks, which may be (at least presently) limiting for its wider application. First drawback of PLD is a difficulty in preparation of films of large size and films of even thickness. The non-uniformity in thickness of large area films is caused by the fact that the laser is focused on a small area (point), plasma plume direction is close to normal direction of the target, and by the  $\cos^n$ -distribution ( $n > 1$ ) of the particles in the plasma plume [66]. There are several methods to overcome this problem: off-axis, rotational/translational and rastered large area PLD techniques or special target geometries – using cylindrical targets [21, 66]. In the

off-axis approach (Fig. 2), the centre of the rotating substrate is offset from the centre of the ablation plume. In case of rotational/translational PLD, the rotating substrate is translated back and forth in one direction with respect to the plume using a computer-controlled vacuum feed through. In rastered PLD, a focused laser beam is reflected by a programmable mirror held in a kinematical mount that allows the beam to be rastered over the entire diameter of the target [21]. Using cylindrical targets, the plasma plume is elongated due to scanning of the target surface across a fixed position of a focussed laser beam [66].

The further disadvantage of PLD is a possible presence of particulates (droplets) in the deposited films, as we have already mentioned. This is a general problem of many evaporation methods. A simplest approach to reduce the number of particulates is to change the deposition parameters (for example to reduce the laser power density); however, at the same time, the advantage of having the high-energy species, which help to produce improved film quality, is lowered. In order to reduce the presence of particulates in films, several mechanical and geometrical techniques (off-axis deposition geometry, substrate bias, velocity filters, electromagnetic shutters, spinning the target at high velocity, plasma discharge etc.) were developed [21]. In ultra-fast PLD process (see, e.g. [6]), the laser pulse energy is lowered in order to decrease the presence of particulates in deposited films. Usually, the PLD is performed using pulses of energy from ~0.1 to several Joules, from UV excimer lasers with repetition rates up to 100 Hz. In case of ultra-fast PLD, lower energy pulses (0.1-1  $\mu\text{J}$ ) with higher repetition rates (up to 100 MHz) are used and deposition rates can reach up to 2.0 nm/s at target-to-substrate distance of 250 mm. One of other techniques for lowering of droplets content is plasma-assisted PLD, where an additional plasma discharge is created between the target and the substrate with or without the presence of a background gas [20, 39]. We have mentioned it earlier.

At last we shall mention relatively high price of solid state or excimer lasers and also high price of the gases, used in them, that shall be changed very often. Using several vacuum systems with one excimer laser can lower the relative price of the facility. The light can be directed into individual vacuum stages by mirrors. The price of individual system is then lowered and becomes close to other evaporating systems.

Pulsed light of excimer lasers can be used not only for deposition, but also for optical information storage [67], waveguides and optical circuits production [9]. In this case, the optically induced changes of the structure and other optical properties (T, R, n) are exploited. The sensitivity of  $\text{As}_{50}\text{Se}_{50}$  photoresists was up to 5 times higher when exposed by excimer laser. The 1000 times larger energy was necessary to obtain the same changes using continuous wave radiation [68]. The effect is probably caused by multiphoton absorption. Laser ablation itself, or when combined with chemical etching, can be used for microfabrication of hard and other materials including chalcogenides.

## 2. Sulphide-based amorphous thin films

Only small number of papers was devoted to PLD of binary, ternary or multinary sulphide thin films [1, 2, 5, 6, 11, 12, 22, 23, 25, 27, 33, 35-39, 41, 42, 44, 49, 70]. This is partly due to the fact that thin films of many sulphides, especially of the system As-S system, which has been studied very intensively due to their interesting photo- and/or thermally-induced changes of structure and/or optical properties (see for example [8, 9]), can be prepared very easy by classical thermal vacuum evaporation. Rode et al. [6] reported fabrication of low loss waveguide films (<0.1 dB/cm at 1550 nm for as-deposited films, <0.2 dB/cm at 1550 nm for fully photodarkened films) from  $\text{As}_2\text{S}_3$  glassy target using ultra-fast PLD technique. Thin As-S films, prepared by ultra-fast PLD, were slightly less photosensitive than the thermally evaporated ones, with average increase of index of refraction  $\Delta n = 0.04-0.05$  [6]. The photosensitivity of deposited As-S films enabled, however, the formation of single-mode channel waveguides. The stoichiometry of such deposited films reflects that one of the target [6]. Lančok et al. [22] found that the As-S film stoichiometry was changed with deposition energy density ( $\text{KrF}^*$  excimer laser). The films were slightly sulfur deficient for energy densities 1.9-3.8  $\text{J}/\text{cm}^2$ , while the films were slightly arsenic deficient for energy densities >4  $\text{J}/\text{cm}^2$ . The stoichiometric films can be deposited at 2.6  $\text{J}/\text{cm}^2$  [22].

A study of photodarkening and Raman spectra of amorphous  $\text{Ge}_{1-x}\text{S}_x$  ( $x \leq 0.62$ ) films, prepared by PLD, was presented by Ogura [23, 41]. He found only a slight difference in composition of the target and the deposited films in the Ge-rich region. Generally, the composition of the deposited films corresponds reasonably well with the stoichiometry of the target as we have mentioned earlier. In the paper [41], Raman spectra of  $\text{Ge}_{1-x}\text{S}_x$ ,  $x \leq 0.62$  at low temperatures (20 K) were reported. The interpretation of the dependence of reduced Raman intensity on  $x$  was done on the base of a fracton model. The fractal dimensions decreased with an increase in  $x$  over the range  $0.2 \leq x \leq 0.62$ . Photodarkening was observed for  $\text{Ge}_{1-x}\text{S}_x$  thin films with  $x > 0.2$  and is enhanced significantly at  $x = 0.5$  [23].

Several papers were devoted also to the study of preparation of ternary (or generally multicomponent) sulfide-based amorphous films by the PLD technique, e.g. of the Ga-La-S, Ag-As-S, Pb-Ag-As-I-S, Cd-Ag-As-I-S, and Ge-Ga-S-Cs-I (pure and doped with  $\text{Pr}^{3+}$  ions) systems, and of other thin films [1, 2, 5, 11, 12, 25, 27, 33, 35-39, 44, 49]. Many of them are used as ionic-selective membranes, ionic selective sensors or as an electronic tongue [12].

It is well known that rare-earth elements and their compounds are generally of low solubility in binary amorphous chalcogenides. In order to increase this solubility, the addition of gallium into glasses is often used [15]. In order to enhance the spectroscopic properties (lifetime, quantum efficiency) of rare-earth ions incorporated in amorphous chalcogenide matrix, alkali halides, especially Cs halides, are often added to the base glasses [71]. A complex composition complicates the preparation of thin films using conventional methods, e.g. using thermal vacuum evaporation, due to low and/or different volatility of rare-earth elements (compounds) and/or different components of chalcogenide glass. The PLD technique, (308 nm or 248 nm laser pulses) allowed preparation of pure and  $\text{Pr}^{3+}$ -doped thin films from  $70\text{GeS}_2-15\text{Ga}_2\text{S}_3-15\text{CsI}$  and  $85\text{GeS}_2-6\text{Ga}_2\text{S}_3-9\text{CsI}$  glasses [1, 2, 37]. The composition of such films prepared by PLD was close to the one of target, only low losses of sulfur was observed [2]. The thickness was uniform within 6%. The presence of  $\text{Pr}^{3+}$  ions in the doped chalcogenide thin film was confirmed by photoluminescence measurements in the  $1.335\ \mu\text{m}$  region due to the radiative electron transitions between  $^1\text{G}_4$  and  $^3\text{H}_5$  energy levels of  $\text{Pr}^{3+}$  ions [2].

The thin film sensors or ion selective membranes can be formed by ternary and multinary chalcogenide systems (e.g.  $\text{PbS-AgI-AsS}$ ,  $\text{CdS-AgI-AsS}$ ,  $\text{Tl-Ag-As-I-S}$ , and others [11, 33-36, 38, 49]). Homogeneous films of such complex chalcogenides (of stoichiometric composition with respect to the used target) were prepared by off-axis PLD technique [33, 35], while classical evaporation methods in such systems failed [24, 49]. Melting of the surface of the target under the illumination by  $\text{KrF}^*$  pulses ( $\sim 1\ \text{J/pulse}$ ) and multiphoton ionization of vapors in plasma were supposed. The power density was of the order of  $10^7 - 10^8\ \text{W/cm}^2$ , and the pulse duration was  $\sim 30\ \text{ns}$ . The prepared films contained some nanometer size crystals as it resulted from studies of transmission electron microscopy. The physicochemical properties of prepared films were in good accordance with the properties of target glasses. The high sensitivity of ion-selective membranes were obtained for determination of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Tl}^+$ ,  $\text{Hg}^{2+}$  and other metal ions (29-60 mV/pX; X = Pb, Cd, Tl, and of Cl [38]). The detection limits are near  $10^{-6}\ \text{mol/l}$  [36].

Thin amorphous films of  $\text{SbSI}$  were grown by PLD on platinized Si substrates in [42]. Annealing at  $250\ ^\circ\text{C}$  can crystallize the films. In the crystals, ferroelectric transition, high dielectric permittivity and pyro-optic effect were found.

Gill et al. [25] prepared stoichiometric Ga-La-S films (laser flux  $\geq 3.5\ \text{J/cm}^2$ ,  $\text{KrF}^*$  excimer laser) with optical properties similar to the ones of bulk target glass. The films were bleached by exposure due to photostructural process, their index of refraction was lowered after exposure by  $\sim 1\%$ . The gratings, written by blue light and e-beam, were prepared from these films. Various optical properties of such Ga-La-S thin films ( $E_g^{\text{opt}}$ ,  $n$ ,  $T$ ,  $R$ ) changed sharply their values due to exposure depending on deposition energy. The increase of deposition energy shifted the absorption edge towards the lower energies, which can be correlated with structural data [27]. The reversible

photobleaching, photo-induced refractive index change, and photodoping effects in PLD prepared Ga-La-S thin films were also found by Youden [5].

### 3. Selenium- or tellurium-based amorphous thin films

The number of papers devoted to study of selenium- or tellurium-based amorphous thin films prepared by PLD is even lower [13, 14, 26, 40, 72-74] than the number of studied sulfides. In some cases, small amounts of selenides or tellurides were added to sulfides. These papers were mentioned in Section 2 and will not be cited again.

One of the first papers dealing with selenides prepared by PLD is the study of amorphous thin films of Ge-Sn-Se by Islam et al. [73]. They found that differences in stoichiometry of the target and films increased with increasing Sn content in target glass. However, laser deposited films had composition much closer to the starting material than the thermally evaporated ones. The GeSe<sub>2</sub> films prepared by PLD had the same composition as the starting material [73].

Pulsed laser deposition of selenium thin films and their characterization was studied by Fernandez-Guasti and co-workers [72]. Selenium amorphous thin films obtained by PLD (using 1064 and 532 nm laser pulses) showed large amount of splashed droplets. The lowering of energy density of the laser beam and/or increasing target-to-substrate distance reduced the density of the droplets on the surface. In order to increase the rate of deposition, an external electric field was applied [72].

Thin films of amorphous GeSe<sub>2</sub> prepared by PLD exhibit non-induced optical anisotropy, which can arise from birefringence [26]. Several-micrometer-thick Ge<sub>0.25</sub>Se<sub>0.75</sub> films for lateral waveguides of quantum cascade lasers have been prepared by Gmachl et al. [40]. Their optical attenuation was low and resulted in an improved overall laser performance.

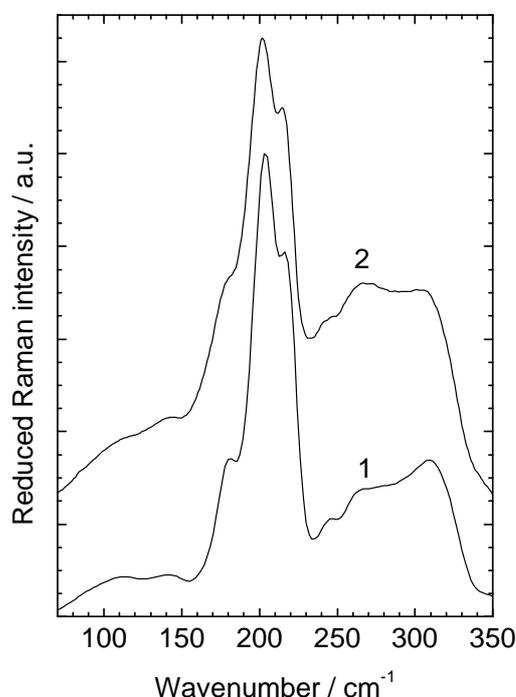


Fig. 3. Comparison of reduced Raman spectra of bulk Ge<sub>30</sub>Ga<sub>5</sub>Se<sub>65</sub> glass (1) with the spectrum of as-deposited Ge-Ga-Se thin film prepared by PLD (2).

A study of Ge-Ga-Se amorphous thin films (pure and rare-earth doped) prepared using PLD was published in our recent papers [13, 14, 74]. The stoichiometry of Ge-Ga-Se films was close to the

composition of target glass of  $\text{Ge}_{30}\text{Ga}_5\text{Se}_{65}$ , nearly independent on energy fluency of used laser beam ( $\text{KrF}^*$  excimer laser) [13,14]. The deposition rates reached the value of 0.21 nm per pulse. According to Raman spectroscopy, the structure of deposited Ge-Ga-Se films was close to the structure of glassy target (Fig. 3). The main structural features are based on corner- and edge-sharing  $\text{GeSe}_4$  ( $\text{GaSe}_4$ ) tetrahedra ( $\text{GeSe}_4 - 201, 310 \text{ cm}^{-1}$ ,  $\text{Ge}_2\text{Se}_{8/2} - 216 \text{ cm}^{-1}$ ). The content of homopolar Ge-Ge, Se-Se, and/or Ga-Ga bonds ( $\text{Ge}_2\text{Se}_{6/2} - 180 \text{ cm}^{-1}$ , Se-Se -  $268, 245 \text{ cm}^{-1}$ ) in deposited films increased with increasing energy density of the laser beam [14]. The index of refraction of as-deposited Ge-Ga-Se thin films increased with increasing energy of the laser beam used for PLD [14]. Exposure of the as-deposited films caused the decrease of the values of index of refraction ( $\Delta n_{\text{max}}=0.11$ ). After annealing of exposed films, values of index of refraction were further decreased ( $\Delta n_{\text{max}}=0.18$ ), and the overall changes of index of refraction reached values of  $\Delta n = 0.2$  (Fig. 4a) [14]. The optical band gap values of Ge-Ga-Se films increased with decreasing energy of the laser beam ( $\sim 1.85\text{-}1.98 \text{ eV}$ , Fig. 4b). After the exposure, the photo-bleaching effect was observed ( $E_g = 1.87$  to  $2.06 \text{ eV}$ , Fig. 4b). The subsequent annealing of the exposed films in Ar atmosphere causes further thermal bleaching ( $E_g = 2.10$  to  $2.25 \text{ eV}$ , Fig. 4b) [14].

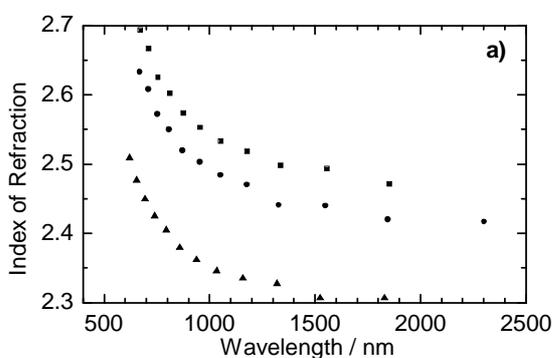


Fig. 4a. Examples of spectral dependencies of index of refraction of as-deposited, exposed, and annealed Ge-Ga-Se amorphous thin films prepared by PLD (energy density of laser beam -  $3 \text{ J}\cdot\text{cm}^{-2}$ ): squares – as-deposited films, circles – exposed films, triangles – annealed films.

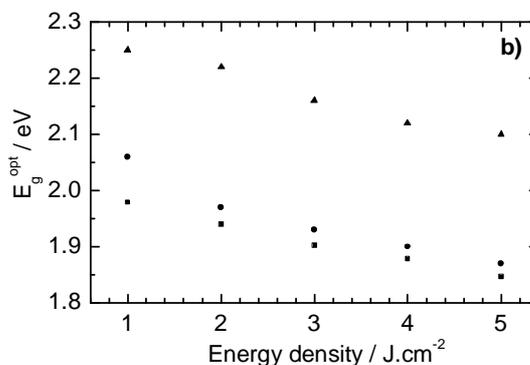


Fig. 4b. Optical band gap dependencies of as-deposited (squares), exposed (circles), and annealed (triangles) Ge-Ga-Se amorphous thin films on energy density of laser beam used for PLD.

Rare-earth-doped selenium-based thin amorphous films, namely  $\text{Pr}^{3+}$ - and  $\text{Dy}^{3+}$ -doped Ge-Ga-Se films, were studied by means of photoluminescence spectroscopy [13, 74]. Two emission bands (1340 and 1610 nm, Fig. 5a) were observed in the photoluminescence spectra (excited with 1064 nm laser light) of  $\text{Pr}^{3+}$ -doped Ge-Ga-Se thin films prepared by PLD in analogy with the luminescence spectra of target glass [13]. Observed emission bands can be assigned to the radiative intra-f electron transitions between energy levels  $^1\text{G}_4 - ^3\text{H}_5$  (1340nm) and  $^3\text{F}_3 - ^3\text{H}_4$  (1610 nm) of  $\text{Pr}^{3+}$  ions, respectively [13]. In the photoluminescence spectra of  $\text{Dy}^{3+}$ -doped Ge-Ga-Se thin films, two emission bands at 1140 and 1340 nm were found (Fig. 5b) [74]. The observed emission bands were connected with the radiative electron transitions  $^6\text{F}_{9/2}, ^6\text{H}_{7/2} - ^6\text{H}_{15/2}$  and  $^6\text{F}_{11/2}, ^6\text{H}_{9/2} - ^6\text{H}_{15/2}$  of  $\text{Dy}^{3+}$  ions, respectively [15, 74]. The intensity of luminescence bands of films prepared by PLD was lower when compared with the target bulk glasses (note that the intensity of emission bands (Fig. 5a, 5b) is normalized for the sake of clarity), which is caused at least partly by the lower pumping efficiency of excited energy levels of rare-earth ions due to lower absorption. The infrared luminescence of  $\text{Pr}^{3+}$ - or  $\text{Dy}^{3+}$ -doped chalcogenide thin films is of large interest for active waveguides and other applications in optoelectronics but the method of preparation must be still improved.

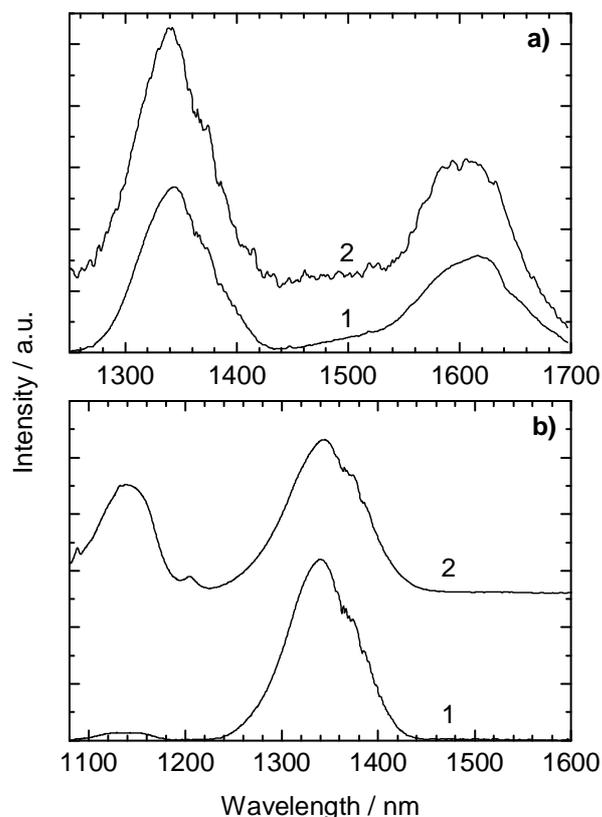


Fig. 5. a) Photoluminescence spectra of  $(\text{Ge}_{30}\text{Ga}_5\text{Se}_{65})_{99.5}(\text{Pr}_2\text{Se}_3)_{0.5}$  bulk glass (1) and of as-deposited thin film prepared from  $(\text{Ge}_{30}\text{Ga}_5\text{Se}_{65})_{99.5}(\text{Pr}_2\text{Se}_3)_{0.5}$  target by PLD technique (2); excitation wavelength 1064 nm; b) Photoluminescence spectra of  $(\text{Ge}_{30}\text{Ga}_5\text{Se}_{65})_{99.5}(\text{Dy}_2\text{Se}_3)_{0.5}$  bulk glass (1) and of as-deposited thin film prepared from  $(\text{Ge}_{30}\text{Ga}_5\text{Se}_{65})_{99.5}(\text{Dy}_2\text{Se}_3)_{0.5}$  target by PLD technique (2); excitation wavelength 1064 nm.

#### 4. Conclusion

The PLD technique is a promising method for preparation of thin films with stoichiometry close to used targets of complex composition. The large advantage of this method is a possibility to deposit at once the volatile and non-volatile parts of target material. The films of complex composition can be thus prepared as well as the films of nearly any material including the non-volatile ones as carbon, diamond, tungsten, oxide refractories, etc. The method seems to be very suitable for doped amorphous chalcogenides and for chalcogenides of binary, ternary, and multinary systems. The advantages and drawbacks of PLD technique for thin film preparation were briefly reviewed and the results obtained with chalcogenide amorphous thin films prepared by PLD were mentioned. The method is relatively new and many processes must be still clarified and many problems must be solved.

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