

## LASER ABLATED AMORPHOUS MULTILAYERS

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*The possibilities of a pulse-laser deposition technology are presented. Periodic Se/Se<sub>85</sub>Te<sub>15</sub>, Se/CdSe and Se/Ge<sub>20</sub>Se<sub>69</sub>Bi<sub>11</sub> nanostructures could be obtained in a Nd-glass laser set-up, suitable for alternative deposition of nanolayers in amorphous state. The parameters for the laser-ablation process in the different materials have been established. The ablation threshold power densities have been defined and the power densities at suitable distances between targets and substrates have been optimized for making layers without drops and with correct composition, as well as multilayers with low disorder in sublayers and interfaces and with pre-established periodicity.*

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### 1. Introduction

Recently, a new class of low-dimensional structures was studied intensively: amorphous multilayers (a-ML) or superlattices with nanometric period (>5 nm) composed of two types of alternating chalcogenide layers [1]. With band-gap engineering new properties can be achieved based on classical effects or on quantum-size effects (QSE). The advantages of the chalcogenides are associated with their low coordination and great flexibility. High quality periodic nanostructures with smooth and parallel sublayers and sharp interfaces, where observation of QSE could be expected, can be obtained only with suitable step-by-step deposition methods, one of which is the pulse-laser ablation method.

The laser ablation was exploited recently for preparation of thin films from a-Si [2], ZnO [3], CdS [4], a-C [5], PbTe [6] and some high-temperature superconductor films [7-12]. Pulsed excimer lasers (operating at wavelengths 193, 248 and 308 nm) [8], CO<sub>2</sub> (10.6 μm) lasers [9] and Nd:YAG (1064 and 532 nm) lasers [10] have been used. Nd:YAG laser radiation was frequency doubled and tripled, but as pointed in Ref. [7] the deposited layers do not show different properties in some cases [11]. Using the IR long pulse (~1 ms) Nd-glass laser, films close to the stoichiometry of the target were obtained [12]. The advantages of the laser ablation method for preparing thin films from complex compounds are the very good stoichiometry, as well as the high rate of film formation. These advantages are most important in the preparation of multilayers, especially those based on amorphous materials.

Up to now the laser ablation method has been used mainly for the preparation of Se/Se-Te ML [13-16]. No preparations of amorphous ML based on other chalcogenide materials, or on tetrahedrally bonded amorphous materials, a-Si:H and a-Ge:H, have been reported.

This paper discusses the results obtained in the preparation of chalcogenide amorphous ML by laser ablation.

## 2. Experimental

For the preparation of amorphous chalcogenide multilayers a pulse Nd-glass laser (1.06  $\mu\text{m}$ ) was used. The pulse duration was  $\sim 1.6$  ms. The energy of a pulse was changed between 6 and 16 J. The power density in an impulse was between 0.5 and  $1.2 \times 10^6$  W/cm<sup>2</sup>. The laser beam was focused ( $f=17$  cm) in a spot with diameter 1 mm on the targets from pressed ( $\sim 100$  Kpound) powdered chalcogenide glasses. The glasses from Se, Se-Te and Ge-Se-Bi alloys were prepared by standard melt-quenching technique from pure (5N) materials. The CdSe was polycrystalline powder from Merk (super-pure).

Two targets were used in a vacuum chamber ( $\sim 10^{-4}$  Pa). The schema of the constructed set up is shown on Fig. 1. It gives the possibility to change the position of the targets (rotating them on  $180^\circ$ ) and to rotate every one target around its own axis. The material of the targets was ablated by laser pulses which follow usually after a pause of 15 s. The thickness of the deposited layers was measured in situ with a calibrated quartz resonator MIKI MSV. The thickness from one pulse was varied usually from  $\sim 0.3$  to  $\sim 3$  nm (the fluctuations due to the pulse laser energy fluctuations were 0.1-0.2 nm). A glass disk was rotated in steps between the substrate holder and the optics through which the laser beam passes, to prevent the last from the ablated materials.

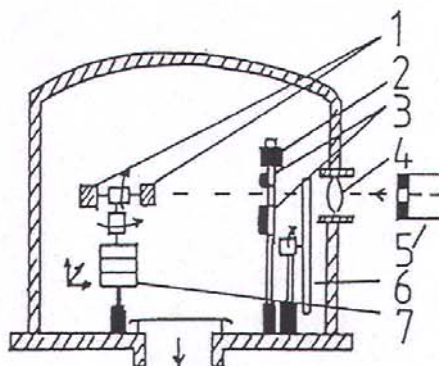


Fig.1 The vacuum chamber set-up used for ML preparation by laser ablation: (1) targets, (2) quartz resonator head, (3) substrates, (4) lens, (5) Nd-laser tube, (6) rotating glass disk, (7) x-y-z table.

The multilayers are deposited on specially cleaned Corning 7059 glass substrates (25:13:1 mm or 7:7:1 mm). In some cases metal plates (polished Al) were used for some complex (electrophotographic) structures which include ML.

The set-up gives also possibilities to change the distance between the substrates and the target and to control the ablation conditions for different materials.

## 3. Results and discussion

The conditions of ablation by pulse irradiation of the chalcogenide materials depend firstly on the laser power density and pulse duration [17], which define the type of vaporization processes, their connection with thermal conductivity or with explosive evaporation from the surface, and, secondary, on the state of the generated plasma. The threshold power density of ablation,  $\Phi$ , depends on the material parameters and their changes during the ablation process:  $\Phi = \rho Q h / (1 - \beta) t_p$ , where  $\rho$  is the density,  $Q$  - the heat of vaporization,  $h$  - the thickness of the absorbing layer,  $\beta$  - its reflection coefficient and  $t_p$  - the pulse duration. Near to the ablation threshold, fine disperse fractions and droplets of the material are ejected. For deposition of ML this regime is unsuitable. That is why an optimal power density has been chosen. This power is 2-4 times higher than the threshold power.

With increasing laser power density the ablation rate and the ionization rate of the plasma increase and, at suitable distances between target and substrates, the distribution of the plasma plume can ensure particles with high mobility on the substrates, necessary for the growth of smooth and homogeneous layers.

The preferable power density of  $5 \times 10^7 - 10^{10}$  W/cm<sup>2</sup> for effective laser plasma vacuum deposition at  $10^{-9} - 10^{-7}$  s pulse duration [17] could be lower when materials with lower evaporation heat and long pulsed Nd-glass laser are used. A decrease of 1-2 order is acceptable if sublayers from Ge<sub>20</sub>Se<sub>69</sub>Bi<sub>11</sub>, CdSe, Se, Se<sub>85</sub>Te<sub>15</sub> are deposited for preparing Ge-Se-Bi/Se, CdSe/Se and Se-Te/Se ML. In the preparation of nanostructures with period higher than 5 nm one have to maintain the sublayer thickness with deviations not greater than 0.1-0.2 nm. Because of the fluctuations in the energy of the laser beam one have to obtain the desired thickness for every one sublayer in more than one pulse of laser ablation. The step-by-step deposition of a sublayer with a low pulse rate ensures the growth of smooth layers, as has been shown by comparing step-by-step and continuous thermal vacuum evaporation [1]. Nevertheless, to achieve the desired thickness one have to use also pulse energies near to the ablation threshold at the end of the sublayer deposition. That is why, to be excluded the hits of droplets, the distance between the target and substrates has been increased and established in the range of 8-13 cm.

Fig. 2 shows the relation between the minimum energy in a pulse of the focused Nd-glass laser beam, needed for extraction of material out of the Se and CdSe targets and to deposit it at distances R between the target and the substrates and the duration of the ablation process at the moment  $t_1$  just after beginning of the deposition and at the moment  $t_2$  at the end of the deposition of a Se/CdSe ML. One can see that: (i) the ablation threshold energy increases with increasing the time in which the target is influenced from the laser ablation process. This can be related to an increase of the density  $\rho$  of the target surface, which means that for the condition necessary to the creation of periodic nanostructures the material is ablated by a process that will have a thermal-conductivity component which melted and glazed the target surface. (ii) This ablation threshold increases with the increase of the distance R at a higher rate after a higher ablation time  $t_2$ . The threshold power density for Se at distances R=12 cm reaches  $7 \times 10^5$  W/cm<sup>2</sup>. At the same condition for CdSe is  $8 \times 10^5$  W/cm<sup>2</sup>.

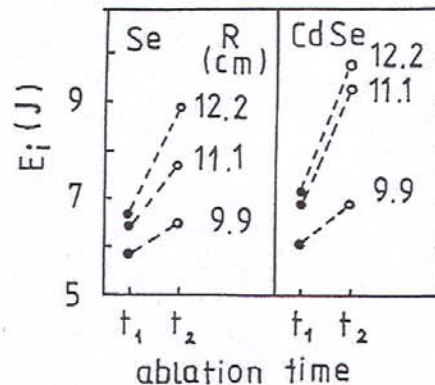


Fig. 2 Threshold energy  $E_i$  of the pulses of the Nd-glass laser beam at time  $t_1$  in the beginning of the ablation from the Se and CdSe targets and deposition on substrates at various distances to the target R, and at time  $t_2$  in the end of the deposition of a Se/CdSe ML.

The assumption that the use of power densities near the ablation threshold, at the end of the deposition of the sublayers, at the chosen distance R, do not damage the periodic nanometric structures is confirmed by the small angle X-ray diffraction (SAXRD) pattern of a Se/CdSe ML, deposited at a distance of ~9 cm. The data on Fig. 3 are obtained in the National Institute of Materials Physics of Romania and extracted from the paper by M. Popescu et al. [18]. Similar data one expects

for the prepared and investigated Se/Se<sub>85</sub>Te<sub>15</sub> ML [1], but well expressed peaks (in the SAXRD patterns) could not be seen because of the little difference between the refraction indices of the sublayer materials.

Here it can be pointed out that the structural state of the sublayers in the mentioned ML is amorphous. The single CdSe films are polycrystalline, but sufficiently thin CdSe layers in the Se/CdSe ML are amorphous as has been shown by XRD measurements at high angles, of ML with CdSe sublayers about 11 nm thick. They do not reveal peaks typical for the crystalline structure [19]. The MLs in [19] are obtained with a rate of ~0.5 nm/s by thermal vacuum evaporation. The laser ablated Se/CdSe ML are obtained with a rate of ~200 nm/s in a pulse. Obviously, higher deposition rates are suitable for the growth of amorphous layers.

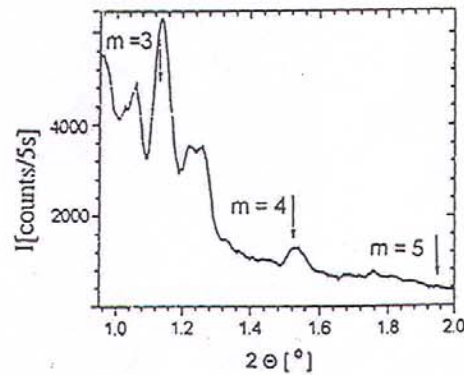


Fig. 3 SAXRD pattern from a laser ablated a-ML Se/CdSe with period 22 nm (14 pairs) deposited at the distance  $R=9$  cm.

The quality of the amorphous layers which enables the realization of periodic nanostructures is conditioned by the shorter time (1.6 ms) in a step, in which usually 0.3-0.4 nm thick layers are deposited, and the pauses (~15 s) between the laser pulses, thus ensuring the time for relaxation of the structure to a stable state. The good quality of the a-ML Se/CdSe is confirmed with photoelectric measurements. Using the Constant Photocurrent Method (CPM) the spectral characteristics of the absorption coefficient  $\alpha$  have been measured. From the exponential range (usually related to the valence band tail states) the Urbach energies,  $E_u$ , have been evaluated. For the best ML there were obtained values of ~52 meV, which are probably in relation with a low disorder in the CdSe sublayers and at interfaces.

One of the advantages of the laser ablation method is the possibility to preserve in the deposited layers the target composition, especially in the case of the materials with high melting temperatures. This problem is important when amorphous multilayers Se/Ge<sub>20</sub>Se<sub>69</sub>Bi<sub>11</sub> of p-n type have to be prepared. The n-type conductivity of the Ge<sub>20</sub>Se<sub>80-x</sub>Bi<sub>x</sub> glasses is only possible if  $x>9$  [20]. The composition of the target cannot be maintained exactly in the usual thermal vacuum evaporation method. We have prepared, for first time, layers from such glasses with the laser ablation method. The properties of the laser deposited Ge-Se-Bi layers have been studied as a function of the deposition conditions. The following conclusions are important: (i) using pulses with mean power densities around  $1.1 \times 10^6$  W/cm<sup>2</sup>, which is higher than the threshold value of  $5 \times 10^5$  W/cm<sup>2</sup>, smooth layers have been obtained. The spectral dependence of  $\alpha$  has been measured and for the optical band gap, defined at  $\alpha=10^3$  cm<sup>-1</sup>, it has been obtained  $E_g^{03}=1.21$  eV. This value is in coincidence with  $E_g^{03}$  for Ge<sub>20</sub>Se<sub>80-x</sub>Bi<sub>x</sub> glasses with  $x>9$  and with n-type conductivity [20]. ( $E_g^0$  value defined from Tauc plot is 1.37 eV). From the electrical measurements the activation energy of the high temperature conductivity (where the polarization effects have been avoided) has been evaluated. The value ~0.8 eV is near to values of n-type layers deposited by r.f. sputtering of similar composition [21]. A confirmation of the n-type conductivity of the layers is the established photo-EMK in structures

with p-type Se layers and Al and C contacts (Al-Ge-Se-Bi/Se-C). (ii) using pulses with power densities lower than  $1 \times 10^6$  W/cm<sup>2</sup>, an increase of  $E_g^0$  is observed. This increase is related to the diminishing of the amount of Bi in the deposited layers [20,21]. In these cases the electrical measurements show a decrease of electrical conductivity. At power densities near to  $5 \times 10^5$  W/cm<sup>2</sup> the conductivity shows a decrease with the factor 7, which could also be related (in accordance with the investigations on Ge<sub>25</sub>Se<sub>75-x</sub>Bi<sub>x</sub> [22]) to a decrease of the Bi content with  $\sim 1.25$  at.%. (iii) The Urbach energy in the layers obtained with the highest pulse energy ( $\sim 14.7$  J) has the lowest value,  $E_u = 56$  meV, which is characteristic to low level of disorder (Fig.4). In layers obtained with lower pulse energy it increases up to  $\sim 95$  meV (the changes in the slope at higher energies are connected with not avoided photo-polarization).

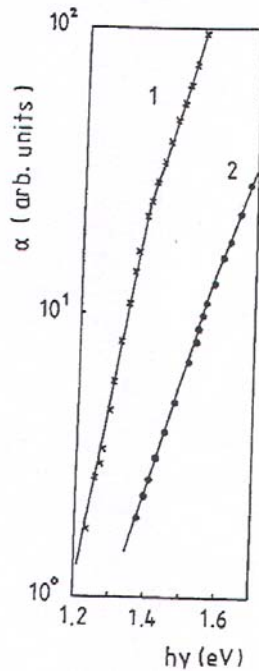


Fig. 4 Spectral dependence of the absorption coefficient  $\alpha$  (obtained by CPM) of Ge-Se-Bi layers ablated with various pulse energies of mean values (1) 14.7 J and (2) 12.5 J.

It can be concluded that, for the preparation of layers from Ge-Se-Bi glasses (with a high melting temperature), it is necessary to use pulse power densities higher than  $1.1 \times 10^6$  W/cm<sup>2</sup>, where the composition is practically identical to that in the target and the layers are more ordered. The control of the composition when Ge-Se-Bi layers are prepared is important not only for p-n ML, but also for other optoelectronic devices with p-n junctions.

The optical measurements of Se/Se-Te ML [1,15] have shown that the optical band gap of the Se-Te sublayers is near to the expected band gap of the glassy target material [23]. The control of the composition during preparation of the Se/Se-Te ML is important for including these multilayers in the generation layers of the electrophotographic photoreceptors sensitive in the near IR spectral region. The first results (similar to those obtained by other methods [24]) give a strong basis to continue the researches in this field.

#### 4. Conclusions

The possibility of a laser ablation technology with a Nd-glass laser set-up was studied. It was shown that, using suitable parameters for the ablation process, it is possible to get layers of pre-established composition and amorphous periodic nanostructures with low disorder in sublayers and interfaces, which makes them interesting for investigations of size effects and for applications in optoelectronic devices.

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