PROPERTIES OF THIN FILMS BASED ON PARAFFIN DOPED CHALCOGENIDES, PREPARED BY PULSE LASER DEPOSITION

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A chalcogenide material of composition $Se_{42}S_{58,}$ doped by 10 wt.% paraffins has been prepared as thin films by pulsed laser deposition. The structural properties of the films have been investigated by X-ray diffraction. Sample stabilization was carried out by annealing at temperatures around 100 ^oC.

1. Introduction

The chalcogenide glasses (e.g. selenium, arsenic sulfides and selenides) are materials sensitive to light. As a consequence they are suggested as convenient media for sensors and optical memories. Various vector and scalar photo-induced phenomena has been observed [1-13], which have no parallel in oxide glasses. The photoinduced effects in selenium-sulphur glass and thick films have been investigated by several research groups. It was proved that the photo-structural effects induced in these materials are accompanied by a significant shift of the absorption edge situated in the red part of the spectrum and change in the refraction index [14]. Due to divalency of selenium and sulphur the chalcogenide glasses exhibit a polymer character with long chain configurations similar to the case of organic polymers. The organic polymers are usually soft materials and, therefore, exhibit easily photoinduced atom displacements (PAD) with corresponding change of the properties of the material. The process is similar to the case of chalcogenide polymeric glasses: the light creates a photoinduced excited state in which the charge is redistributed. As a result, there is new polarization in the structure that induces specific atomic displacements. Due to the poor stability of polymers, PAD may lead to not only a change in physical structure bat also a change in the chemical structure and composition. The magnitude of PAD in inorganic glasses is much smaller than in organic polymers. The flexibility of the structure around the excited atom is the crucial parameter to be considered in designing new materials with desired properties. While the organic polymers show high photo-induced effects and low stability, the inorganic polymers (chalcogenides) exhibit low photo-induced effects and good stability. This observation leads Jain [15] to propose the development of novel chalcogenide glass – organic polymer materials, which would combine the advantages of both components on molecular scale.

Pulsed laser deposition is a modern method to deposit thin homogeneous and stoichiometric films started from a solid target. This method has been previously used to prepare thin films of oxides [16], semiconductors [17], superconductors and optical glasses [18]. Recently the method was applied to chalcogenide glasses [19]. The first report on the application of the PLD method to the preparation of Se-S films was given in [20].

This paper show the results of a study on preparation of thin chalcogenide Se-S films doped by paraffins and on the structural properties before and after a mild thermal annealing, carried out

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with the purpose to stabilize the composition, viewed the possible applications in the development of an optical memory.

2. Experimental

Bulk samples of inorganic polymer of the eutectic composition in the system Se-S ($Se_{42}S_{58}$) doped by 10 % wt. paraffins were prepared by mixing the reagent grade components (Selenium Hoboken 99.999, Sulphur 99.9 Romanian Trade Mark and technical Parraffins, Petrochim Ploieşti Romania) in an evacuated ampoule. Gentle heating at 150 ^{o}C (the softening temperature of the eutectic composition is $T_g = 105$ ^{o}C) was carried out and the sample was maintained for half an hour with continuous agitation of the ampoule in order to get a homogeneous mixing. The cooling of the ampoule containing the melt was made in air. After cooling, the ampoule was open and conveniently chunks of materials have been used as targets in pulsed laser deposition. The bulk material was investigated by X-ray diffraction. The X-ray pattern shows an amorphous background and several line superposed on it. The crystalline compound Se_3S_5 was identified. This result demonstrates the stoichiometry of the ingot, regarding the eutectic composition prepared in the ampoule.

The pulsed laser deposition was performed with a KrF* excimer laser. The laser source generated pulses having the wavelength $\lambda = 248$ nm with pulse duration $\tau_{FWHM} > 20$ ns and 2 Hz repetition rate. The pulses were focused on the target through a MgF_2 cylindrical lens with the focal length of 30 cm. The incidence angle to the target was 45°. The laser spot was set within 4.2 and 6.4 mm^2. The maximum output energy was 85 mJ/pulse. The fluence was ~ 22 J/cm^2. During laser irradiation brightly colored plume plasma was observed. The shape of this plume is forward directed and slightly divergent. The experiments were performed in a stainles steel vacuum chamber, which was evacuated down to 1-7 $\times$ 10^{-3} Pa. The target was rotated with the frequency of 0.4 Hz during PLD deposition. The substrate for film deposition was a (111) oriented silicon wafer placed parallel to the target surface and situated at a distance of 2-5 cm. The number of pulses applied during deposition process was 15 000.

The film obtained by PLD looks homogeneous, bright and without defects.

The photoinduced effect in the films and the characterization on the optical recording facility, as well as the resolution of an optical memory was tested by using a YAG-Nd laser with t = 10 ns pulse duration (the working regime of the laser was: nanopulse (14 mJ/pulse) and double pulse (28 mJ/pulse), $\lambda = 1064$ nm). A Leitz-Orthoplan-pol microscope was used to this purpose.

3. Results

The properties of the PLD films mentioned above has been measured firstly by ellipsometric method. A thickness of 2.8 micrometers has been determined and a refractive index of 2.5 at 700 nm wavelength, in agreement with the results known from literature.

X-ray diffraction measurements have been performed in two diffractometers: a TUR M62 and a Seifert XRD-7 FPM diffractometer provided with copper target X-ray tubes. A proportional detector and step scan mode have been used during measurements. Automatic recording of the intensity has been made. The time of accumulation of the scattered quanta was 20 seconds per measuring angle. The angular step was set at 0.2 ^{o} (2θ).

The X-ray diagram of the as-prepared thin film shows an amorphous character (see Fig. 1a). The amorphous phase is evidenced by three broad peaks situated at ~25°, ~54° and 87°. No crystalline phase is presented in the film.
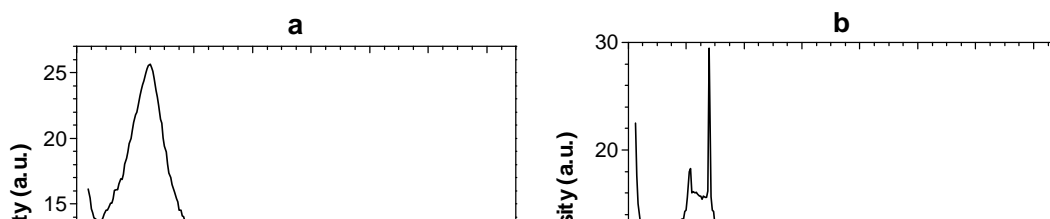
Fig. 1. a. the X-ray diffraction pattern of the as-prepared thin film $Se_{42}S_{58}$ doped by paraffins.
b. the X-ray diffraction pattern of the annealed film $Se_{42}S_{58}$ doped by paraffins.

The chalcogenide PLD films were subsequently annealed in order to stabilize the structure. Taking into account the low softening temperature of the film we have performed the annealing at 95 ± 5 ^{o}C, in argon atmosphere (+10 % H), for half an hour. The gas pressure was ~500 mbar. After annealing the films were cooled very slowly (~3 deg/min) and finally were exposed to the normal atmosphere. The X-ray diffraction pattern of the annealed film was recorded in exactly the same conditions as the fresh (unannealed) film. The X-ray diffraction pattern on the annealed film (Fig. 1b) shows that part of the film has crystallized in a minor phase with very small crystallites (nanometer size) of average size ~20 nm.

The phase was not clearly identified. It is possible that a combination of $Se_{47}S_{53}$ phase (ASTM file 41-1316) and some other phase Se-S was formed. The additional peak observed on the diagram is due to the (111) plane of the silicon wafer substrate. It is possible that, during the stabilization treatment, part of paraffins be eliminated and a phase separation occurred. If this hypothesis is valid, then the detailed study of the radial distribution function of the amorphous phase before and after heat treatment will allow for getting information on the phase change.

The X-ray diffraction curves were processed in order to get the radial distribution functions, useful for the structural information regarding the atom scale arrangement in the films.

Fig. 2 and 3 show the radial distribution functions and the difference curves.
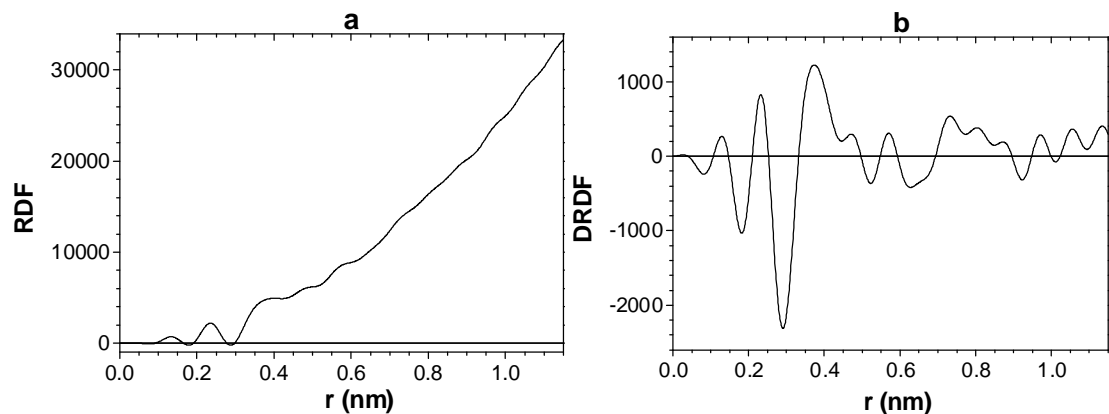

Fig. 2. Radial distribution function (RDF) (a) and difference radial distribution function (DRDF) (b) in fresh PLD deposited thin films of hybrid chalcogenide-paraffin amorphous material.
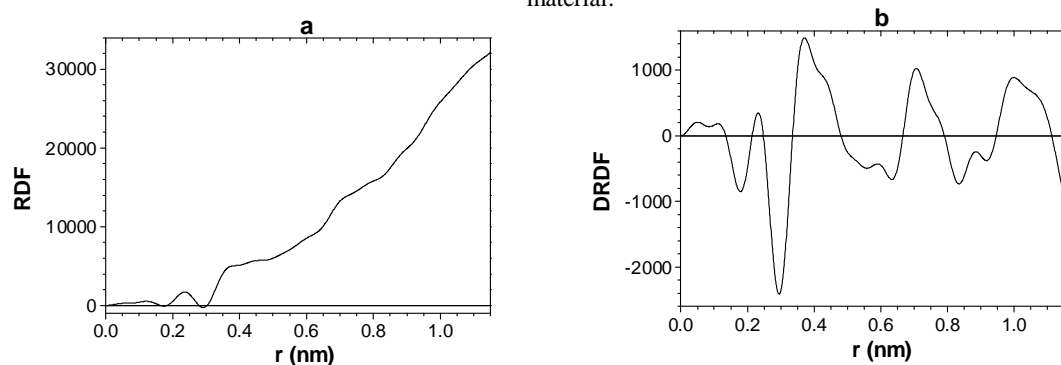
Fig. 3. Radial distribution function (RDF) (a) and difference radial distribution function (DRDF) (b) in annealed PLD deposited thin films of hybrid chalcogenide-paraffin amorphous material.

From the radial distribution functions and difference radial distribution functions calculated before and after annealing it was possible to extract the main structural characteristics of the films. Table 1 shows the main parameters of the films before and after annealing.

Table 1. Structural parameters of the paraffinated selenium-sulphur films.

Structural parameter	Fresh Se-S paraff. film	Annealed Se-S paraff. film
r_1(Å)	2.325	2.319
rms(r1) (Å)	0.537	0.564
area under r_1 peak (e.u.)	1014	875
r_2(Å)	3.735	3.708
r_3(Å)	4.715	4.326
r_4(Å)	5.702	5.905
r_5(Å)	7.323	7.065

The areas under the first peak in RDF shows that in both fresh and annealed films the structural bonding specific to alternating di-valent atoms of selenium and sulphur is preserved (Fig. 4). Nevertheless some differences are apparent. In the fresh films the coordination of the chalcogen is situated near 2, corresponding to the area of 1014 in electron units.

This is somewhat lower than the case of the model with Se and S alternating chains (996) and much lower than in the case of phase separated state of the material (1268). This lower value can be attributed to the presence of parrafins that decrease the length of the chains selenium-sulphur.

As concerning the annealed films, the area under the first peak decreases up to 875 e.u. and this indicates that the Se-S long chains break, while the final configuration is determined, at least partially by the interposition of the parraffin chains, and long alternating Se-S.
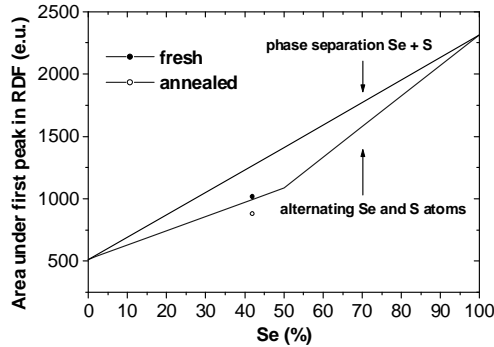

Fig. 4. The area under the first peak of the thin film of hybrid chalcogenide-paraffin amorphous material.

In the same time the chalcogen organization gives rise to a minute amount of crystalline $Se_{47}S_{53}$ (ASTM file 41-1316).

The variation of the optical film properties during light irradiation gives the possibility to record the information on thin hybrid chalcogenide-paraffin films.

Some experiments on the possible change induced by light in the amorphous hybrid films have been performed. Persistent change of light absorption under the influence of laser pulses warrants the use of the films as optical memory elements.

4. Conclusions

For the first time thin films of chalcogenide/paraffin amorphous solid have been prepared by pulsed laser deposition. The films are homogenous and they become stable in time after a short treatment under T_g. The stabilized films contain minor nanometric size crystalline phases of composition $Se_{47}S_{53}$.

Acknowledgement

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