Journal of Optoelectronics and Advanced Materials Vol. 5, No. 5, 2003, p. 1081 - 1084

PULSED LASER DEPOSITION OF SELENIUM-SULFUR DOPED BY PARAFFINS

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Hybrid polymer based on selenium-sulphur doped by paraffins has been deposited by pulsed laser deposition. The properties of the thin films were investigated. Sample stabilization was carried out by annealing. A nano-crystalline fraction was obtained in the films annealed at 100 ^{o}C. The structure of the nanocrystals corresponds to the Se_3S_5 crystallographic form. The films exhibit optical memory properties and are suggested for use in optical phase change memories.

(Received July 15, 2003; accepted August 28, 2003)

Keywords: Chalcogenide, Paraffin doped Se-S, Thin film, Pulsed laser deposition, Amorphous composite

1. Introduction

The glasses based on chalcogens (e.g. selenium, sulfides or selenides of germanium arsenic or antimony) are very sensitive to light, especially if the photon energy is equal to the band gap of the material. A variety of vector and scalar photo-induced phenomena has been observed [1-13], which have no parallel in oxide glasses. Due to divalency of selenium and sulphur, the chalcogenide glasses exhibit a polymer character with long chain configurations, similarly to the case of the organic polymers.

The organic polymers are usually soft materials and, therefore, they easily exhibit photoinduced atom displacements (PAD) with corresponding change of the properties of the material. The process is simlar 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, which then induces specific atomic displacements. Due to the generally poor sterical stability of the polymers, PAD may lead to not only to a change in physical structure but also to 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 structural stability, the inorganic polymers (chalcogenides) show lower photo-induced effects but a fairly good structural stability. This observation lead Jain [14] to propose for optimum material properties the development of a new composite material based on chalcogenide glass and organic polymer, with a connectivity assumed to be of type 2-2, which might combine the advantages of both components at 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 [15], semiconductors [16], superconductors and optical glasses [17]. The method is well suitable for the preparation of hybrid homogeneous and stoichiometric films starting from targets that contain organic components embedded into inorganic bulk material [18].

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In this paper we report the first results on the preparation and properties of a new material based on the combination of organic polymer (paraffin) and inorganic polymeric glass (selenium-sulfur alloy).

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 in an evacuated ampoule. Gentle heating at 150 ^oC was carried out and the sample was maintained for one hour with continuous agitation of the ampoule in order to get a homogeneous mixing. The cooling was made in air. After cooling, disc shaped target for pulsed laser deposition was cut from the ingot. The sample was firstly investigated by X-ray diffraction. The X-ray pattern shows an amorphous background and several lines superposed on it. The crystalline compound Se_3S_5 was identified. This result demonstrates the stoichiometry of the ingot.

The pulsed laser deposition was made with a KrF^* excimer laser (248 nm wavelength of the emitted UV pulse, pulse duration >20 ns, at 1 Hz repetition rate). The pulses were focused on the target through a MgF_2 cylindrical lens, with a focal length of 30 cm. The incidence angle to the target was 45^o. The area of the laser spot was set within 4.2 to 6.4 mm^2. The maximum output energy was 85 mJ/pulse. During laser irradiation a brightly colored plume/plasma was observed. The shape of this plume is forward directed and slightly divergent. The holder with the chalcogenide target was placed in a stainless vacuum chamber, which was subsequently evacuated down to 1-7 × 10^{-3} Pa. The target was rotated with the frequency of 0.4 rot/min during PLD deposition. The substrate for film deposition was a (111) oriented silicon wafer placed on a molybdenum-heating block, parallel to the target surface and situated at a distance of 2-5 cm below it. The total number of pulses applied during the deposition process was 15 000.

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

3. Results

The PLD film of the composition 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 the literature.

X-ray diffraction measurements of the films have been performed on a Seifert XRD-7 FPM diffractometer provided with a copper target X-ray tube. 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 to 0.2 ^{o} (2 theta).

The X-ray diagram of the as-prepared thin film shows an amorphous character (see Fig. 1). The amorphous phase is evidenced by three large peaks situated at ~25^o, ~54^o and 87^o. No crystalline phase could be detected in the film.

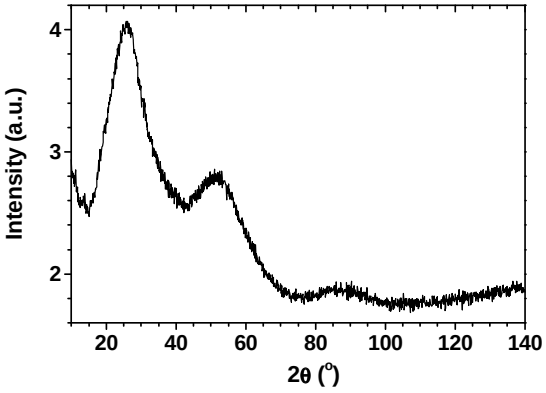

Fig. 1. The X-ray diffraction pattern of the as-prepared thin film $Se_{42}S_{58}$.

The chalcogenide PLD film was subsequently annealed in order to stabilize the structure. Taking into account the low softening temperature of the film (~ 110 ^{o}C) we have performed the annealing at 95 ±5 ^{o}C, in argon atmosphere (+10 % H), for about 30 minutes. The gas pressure was 5×10^{-3} mbar. After the annealing treatment, the film was cooled very slowly and finally was exposed to normal atmosphere. The X-ray diffraction pattern of the annealed film was recorded in exactly the same conditions as that of the fresh (not annealed) film. The general X-ray diffraction pattern of the annealed film (Fig. 2a) shows that part of the film has crystallized in a minor phase, with very small crystallites, with an average crystallite thickness of 14 nm for the direction perpendicular to (210) planes, and 25 nm for that perpendicular to (221) planes. The phase was identified as monoclinic selenium (α-Se). The additional peak observed on the diagram is due to the (111) plane of the silicon wafer substrate.

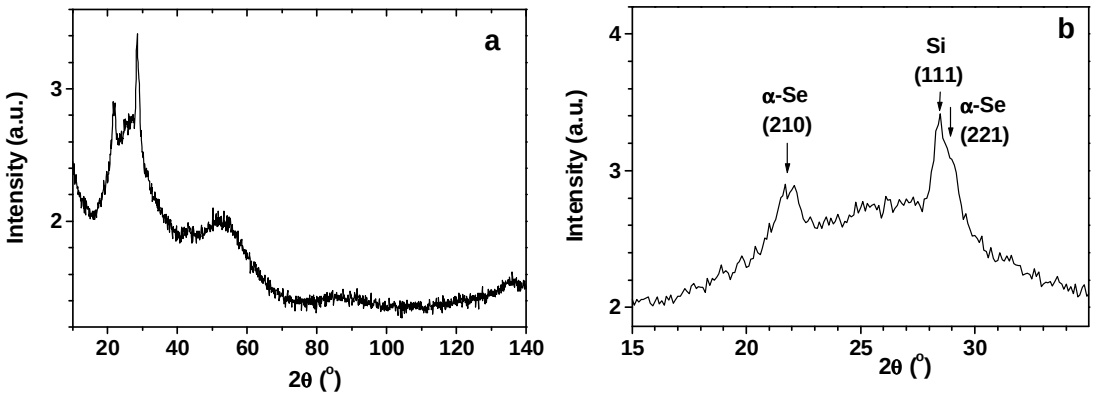

Fig. 2. The X-ray diffraction pattern of the annealed film $Se_{42}S_{58}$. a. full diagram; b. X-ray diagram in the region of the crystalline peaks (enlarged).

It is possible that during the stabilization treatment, paraffin to be eliminated and a phase separation of the remained matrix to occure. 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 to get information on the phase change. The physical properties of the film (as e.g. photoconductivity, refractive index, etc...) are supposed to be different from those of the fresh film.

Further results on the structure of the two amorphous phases observed in the chalcogenide film before and after annealing will be reported elsewhere after the processing of the X-ray diffraction curves and calculation of the radial distribution curves.

Photoconductivity properties of the chalcogenide film doped by paraffins are under study. The variation of the optical film properties during light irradiation might serve as a mean to record the information on thin hybrid chalcogenide-paraffin films.

Experiments on the possible change induced by light in the amorphous composite films have been performed. Non volatile 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 composite 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 thermally stabilized film contains a minor nanometric size crystalline phase of monoclinic selenium (α -Se).

Acknowledgement

The partial support of the Ministry of Education, Research and Youth under Contract No. 23/2001 CERES is kindly acknowledged.

The author is grateful to Prof. I. N. Mihailescu and his group of research for the preparation of the PLD films.

Last but not least, the continuous interest of Prof. M. Popescu is kindly acknowledged.

Thanks are due to Dr. I. Himcinski from the Technical University of Chemnitz, Germany, for the ellipsometric measurements, and to Dr. Ivan Kaban for the help with the thermal annealing.

Special thanks are due to Prof. W. Hoyer who helped with his group (Dr. H. Giegengack, Dr. A. Pohlers) the X-ray diffraction measurements.

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