Materials Letters 142 (2015) 229–231

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Thin films of amorphous Ga_2S_3 and rare-earth sulphides

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ARTICLE INFO

Article history:
Received 18 September 2014
Accepted 4 December 2014
Available online 13 December 2014

Keywords:
Amorphous thin films
Spark Plasma Sintering
Pulsed Laser Deposition
Femtosecond laser irradiation

ABSTRACT

The aim of this research is to prepare amorphous thin films of undoped gallium sulphide and doped with rare-earth sulphides, of rare-earth sulphides and to investigate their physical properties. We have prepared thin amorphous films of Ga_2S_3, EuS, Er_2S_3, Gd_2S_3, and Ga_2S_3 doped with rare-earth sulphides (Ga_2S_3:EuS, Ga_2S_3:Er_2S_3, Ga_2S_3:Gd_2S_3) by Pulsed Laser Deposition (PLD). The corresponding targets for preparation of amorphous thin films were obtained by Spark Plasma Sintering (SPS) from commercially available powders of binary sulphides. The structural results for the undoped and doped Ga_2S_3 thin films indicate a packing of disordered layers similar to that of amorphous As_2S_3. Femtosecond laser irradiation of the Ga_2S_3 thin films shows a photoexpansion effect at low laser power (85–100 mW) and an ablation effect at higher laser power (above 105 mW). The threshold between low power and high power pulses is situated at higher value for Ga_2S_3 (100 mW) in comparison with the case of As_2S_3 thin films (20 mW).

1. Introduction

Chalcogenide glasses based on Ga_2S_3 have interesting applications in optics and optoelectronics [1] such as infrared and mid-infrared lasers [2], fiber optics amplifiers [3]. They can be drawn into optical fibers [4], can form waveguides [5] or can be doped by high concentrations of RE-ions [6]. Sulphide glasses are wide band gap semiconductors (1.5–3.6 eV) making them promising candidates for optoelectronics and photovoltaics.

The best known RE gallium-sulphides glasses are the gallium–lanthanum-sulphide glasses which have been proposed as RE hosts for 1.3 μm optical amplification devices [7]. Recently Pompilian et al. [8] have prepared and investigated amorphous thin films of Er- and Pr-doped Ga–La–S.

Using the same techniques (SPS and PLD), Yang et al. [9] have obtained high-quality crystalline thin films of the ferromagnetic insulator europium (II) sulphide (EuS).

We report in this paper the preparation and properties of amorphous thin films based on undoped gallium sulphides and doped by rare-earth sulphides, and on rare-earth sulphides.

2. Materials and methods

Ga_2S_3 (purity 99.99%) and rare-earth sulphides powders (Alpha-AESAR and CHEMOS GmbH) were used to prepare mixtures under ambient conditions by manually grinding for 360 s in an agate mortar. These mixtures with compositions of $(Ga_2S_3)_{0.95}(Re_xS_y)_{0.05}$ at%, (where Re_xS_y = EuS, Er_2S_3 and Gd_2S_3) were used to prepare disc-shaped bulk samples by SPS. Using the same technique, additional disc-shaped bulk samples of EuS, Er_2S_3 and Gd_2S_3 have been prepared.

For Spark Plasma Sintering we have used a commercial SPS machine FCT Systeme GmbH—HP D 5, Germany. In the SPS technique a pulsed current and a uniaxial pressure on punches of a mould system are simultaneously applied. The initial vacuum in the SPS furnace was 40 Pa. The uniaxial pressure applied on punches was 60 MPa. The heating rate was 100 °C/min and the temperature rise up to 900 °C when this temperature was maintained for 5 min. A pulsed current pattern of 12-on/2-off pulses was applied, with a 3 ms period. The total time of one sequence was ~0.04 s. The operating voltage and the peak current were up to 5 V and 1600 A, respectively.

The sintered ceramic disks have been used as targets for Pulsed Laser Deposition (PLD) of thin films. During the laser ablation process, the glass and silicon substrates were kept at room temperature and continuously rotated. The targets were irradiated with a KrF* laser, model COMPexPro 205, Lambda Physics-Coherent (λ = 248 nm, τ_{FWHM} = 25 ns) that operated at a repetition rate of 10 Hz and at a fluence of 3 J/cm^2.

The thin films have been studied by X-ray diffraction (XRD), atomic force microscopy (AFM), ellipsometry, and optical absorption spectroscopy.

To obtain the X-ray diffraction curves of the thin films we used a Bruker A8 Advanced diffractometer provided with CuKα target tube, scintillation counter, Göbell mirror and Asymmetric Channel-cut (ACC)

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http://dx.doi.org/10.1016/j.matlet.2014.12.028
0167-577X/

Ge (220) to get a parallel monochromatic beam. The fixed incidence angle was 0.6° in detector scan geometry and the counting time per step was of 64 s.

The optical characterization of the thin films was made with the help of a Woollam Vertical-Variable Angle Spectroscopic Ellipsometer (V-VASE). Measurements were performed from UV to near infrared (275–1770 nm), at three different angles of incidence (AOI) of 45°, 60° and 75°.

The optical transmission measurements have been performed by using a spectrophotometer UV-Vis-NIR Carry 5000.

Atomic force microscopy (AFM) topography images were obtained by means of SPM-NTegra Prima AFM (NT-MDT), operated in semi-contact mode, using an NSG 01 cantilever (resonance frequency: 83–230 kHz, elastic constant: 1.45–15.1 N/m), scan rate 1 Hz.

A standard laser micro-processing setup was used for producing microstructures (hillocks or hole) on Ga_2S_3 thin film. The laser source was a femtosecond oscillator Synergy Pro with 800 nm central wavelength, 15 fs pulse duration, 80 MHz repetition rate, and 5 nJ maximum energy per pulse. To focus the laser beam, a NIR Mitutoyo microscope objective with 0.5 numerical apertures and 100 × magnification is used. In the focal plane the estimated diameter spot is 3 μm. The laser power, which was varied from 20 to 120 mW, is controlled using a half-waveplate and two polarisers in reflection to minimise the temporal dispersion. At each point the irradiation was performed for 300 ms.

3. Results and discussion

X-ray diffraction: The X-ray diffraction diagrams of the thin films are shown in Fig. 1b–h. All the PLD prepared films are amorphous. One observes in Fig. 1b, c, e, g (Ga_2S_3, Ga_2S_3:EuS, Ga_2S_3:Er_2S_3, Ga_2S_3:Gd_2S_3) a well-developed first sharp diffraction peak (FSDP), as can be seen in the case of As_2S_3 amorphous thin film (Fig. 1a). This speaks in favour of the quasi-bidimensional layers with disordered configuration, similar to the structure found in As_2S_3 glass and thin films.

Ellipsometry: The results of the ellipsometric measurements are shown in Fig. 2. The refractive index for the Ga_2S_3 is higher than 3.0 between 308 nm and 378 nm. The extinction coefficient (k) is situated in the range 0–1.5.

Optical absorption: From the optical transmission measurements, $T(E(\text{eV}))$ where E(eV) is the energy of light quanta expressed in electronvolts, we obtained the optical band gap for the prepared sulphide amorphous thin films, using the plot $(Abs)^{1/2} = f[E(\text{eV})]$, where $Abs = \ln(100/T)$. Table 1 shows the values of the optical band gap of the gallium sulphide and of the rare-earth sulphides in comparison with the Ga–La-S prepared and studied in [8].

Femtosecond laser pulse irradiation and nanostructures formation in amorphous Ga_2S_3 thin films: By irradiation of an amorphous Ga_2S_3 thin film (1.7 μm thickness) with a femtosecond laser spot of micrometer size, which has the power between 85 mW and 100 mW, nanostructures in the form of hillock are formed, as observed for amorphous As_2S_3 thin films [10].

A polynomial fitting of the profile (obtained by atomic force microscopy) of the hillocks (Fig. 3a) was performed: $z(r) = \sum_{i=1}^{n} p_i r^{n-i+1}$, where $n = 10$ is polynomial degree, p_i are the fitting polynomial coefficients, r is the polar radius ($r = \sqrt{x^2 + y^2}$) and z is the height (z-coordinate). The volume of the shape is $V = 2\pi \int_0^{r_{max}} rz(r)dr$, where r_{max} is the maximum polar radius. The expansion coefficient (as percentage) is defined as $\varepsilon_V = (100V/\pi r_{max}^2 h)$, where h is the depth of the original layer. For the power of 100 mW of the femtosecond laser pulse $V = 0.077\ \mu m^3$, $\varepsilon_V = 2.45\%$.

In Fig. 3b is shown a comparison between profiles of the hillocks performed with the maximum possible power of femtosecond

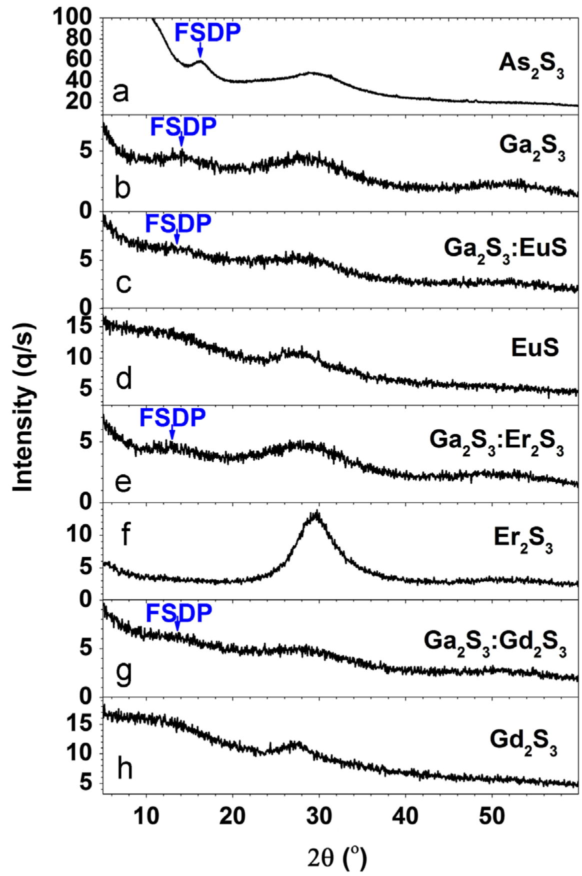

Fig. 1. X-ray diffraction diagrams of (a) As_2S_3 amorphous thin film and (b)–(h) the investigated amorphous thin films based on various sulphides. The first sharp diffraction peak (FSDP) is evidenced on some diagrams.

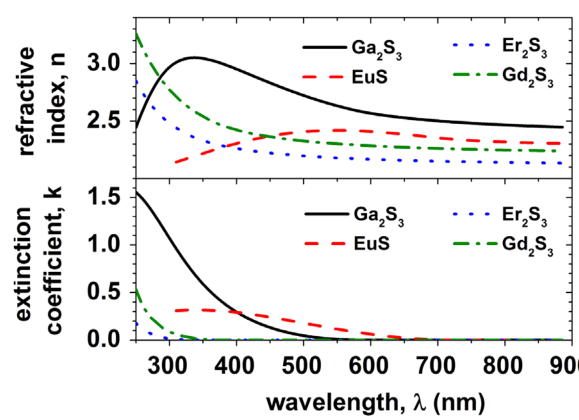

Fig. 2. Refractive index (n) and extinction coefficient (k) for amorphous thin films of Ga_2S_3, EuS, Er_2S_3 and Gd_2S_3.

Table 1
Optical band gap (E_g) of some gallium and RE sulphides amorphous thin films.

Sample	E_g (eV)
Ga_2S_3	2.17
EuS	1.52
Gd_2S_3	3.02
Er_2S_3	3.64
Ga–La-S:Er [8]	1.6–1.8
Ga–La-S:Pr [8]	1.9–2.1

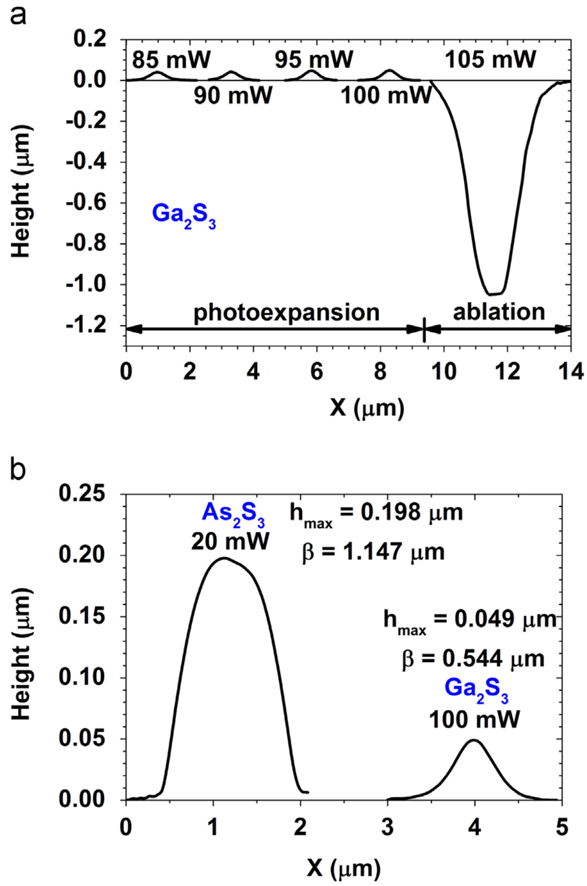

Fig. 3. (a) The profiles of the hillocks performed by irradiation with different powers of femtosecond laser pulse (85 mW, 90 mW, 95 mW, 100 mW) and of the hole performed by irradiation with 105 mW. (b) Comparison between profiles of the hillocks of As_2S_3 [10] and of Ga_2S_3.

laser pulses in the case of As_2S_3 [10] (20 mW) and of Ga_2S_3 (100 mW). Above these thresholds ablation occurs by femtosecond laser irradiation (Fig. 3a).

4. Conclusions

The Spark Plasma Sintering proved to be the most suitable method for obtaining the disk shaped PLD-targets. Thin amorphous films based on Ga_2S_3 and RE-sulphides were obtained by Pulsed Laser Deposition on glass and silicon substrates. XRD diagram of amorphous Ga_2S_3 thin film speaks in favour of a structure with disordered layers, similar to the structure of the amorphous As_2S_3 thin films. The refractive index of amorphous Ga_2S_3 thin film is 2.95 at 400 nm wavelength. A photoexpansion effect in the Ga_2S_3 film irradiated by femtosecond laser pulses was observed for a laser power between 85 mW and 100 mW. The maximum photoexpansion effect (2.45%) was observed for 100 mW. The photoexpansion effect for Ga_2S_3 is lower than the one observed for As_2S_3 (5.11%). Two regimes of irradiation have been revealed, similar to those in As_2S_3 films. The threshold between these two regimes is situated at a higher value of the pulse power (100 mW) than for As_2S_3 amorphous films (20 mW).

Acknowledgement

The authors thank S. Miclos and D. Savastru for the calculation of the photoexpansion value and A. Balan for the AFM measurements. They kindly acknowledge the financial support of the Ministry of National Education (Romania) in the frame of the Project NANOVISMAT PN2-162/2012.

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