Available online at www.sciencedirect.com

SciVerse ScienceDirect

Physics Procedia 44 (2013) 45 – 51

Physics Procedia

10th International Conference Solid State Chemistry, Pardubice, Czech Republic

Photo-induced Mass Transport in Thin Films of Amorphous As_2S_3

Ugis Gertners* Janis Teteris

Institute of Solid State Physics, 8 Kengaraga Str., LV1063, Latvia

Abstract

In this report direct photo-induced formation of surface relief gratings (SRG) in thin layers of arsenic sulfide (As_2S_3) are shown. This anisotropic light-induced mass transfer phenomenon has been discussed with the special attention focused on the polarization and intensity of the corresponding light. The experimental setup for the SRG recording is straight-forward consisting of ~10μm optical slit through which an unfocused beam of light is projected on the surface of sample. The evolution of surface relief in dependence from the recording time and polarization has been investigated in detail. The processes of SRG formation and mass transfer which are based on the photo-induced plasticity have discussed.

Selection and/or peer-review under responsibility of the Organisation of the 10th International Conference on Solid State Chemistry.

Keywords: Amorphous chalcogenide films; AFM; Electric field; Surface relief; Polarization

1. Introduction

Due to the wide range of light induced anisotropic changes of chemical properties, fluidity, viscosity, absorption and refraction (birefringence) [e.g., 1, 2] amorphous chalcogenides are very attractive for a multiple patterning. These changes in a resist material enable a selective removal of regions on a thin film or in the bulk of the illuminated resist by developing and etching. This chemical process is rather complicated requiring various developing solutions (etchants) for different resist materials. Obviously this

* Corresponding author. Tel.: +371 28751557
E-mail address: gertners@gmail.com.

1875-3892
Selection and/or peer-review under responsibility of the Organisation of the 10th International Conference on Solid State Chemistry.
doi:10.1016/j.phpro.2013.04.006

can turn out to be a bothersome process lowering the overall efficiency of the surface-relief element production process (increased processing time and costs). The demand of lower cost surface-relief elements (grating-based resonators or filters for waveguides, diffractometers, spectrometers, etc) is one of the main driving forces for the investigation of direct light-induced relief formation on the surface of thin amorphous chalcogenide As_2Se_3 films, which was pioneered by the Chomat's et al in 1976 [3]. In fact due to the constant advancements in the field of lasers and related optics the interest about the interaction of light and matter is growing exponentially. The most common techniques for fabricating and investigating these surface-relief gratings involve an interferometric or holographic exposure by laser with the wavelength near to the band gap of the material.

In the last few years researchers have been studying different kinds of light induced deformations in the light sensitive materials. The direct surface-relief formation during the holographic recording process [4-6] confirms the polarization dependent mass transfer. There are a wide range of techniques used for an interpretation and investigation of this polarization-driven mass transfer. The interpretation of surface-relief forming processes in the situation of lens based setup [e.g., 7, 8] is not fully thorough. In this case during the illumination a continuous mass transfer occurs, thus the adjusted focus continuously moves into or out of the matter, which might cause an incorrectly interpretable results (as shown in the [9]). To minimize the error caused by the intensity gradient in the normal direction (the consequence of focused light) the light has to be uniformly distributed in the normal direction of initial surface. There is a group of experiments where it has been achieved: the application of contact mask [10, 11], anisotropic deformation of free standing flakes or multiple cracks on the thin film caused by the uniform illumination [12] and coherent beam interference experiments [e.g., 2, 13]. In all the previously mentioned cases it was observed that the formation of surface reliefs is substantially affected by the polarization state of recording beam(s) (a detailed dependency for a holographic recording can be found in [2]). Therefore, there is a reason to believe this is a photoinduced birefigence related process which is being investigated in chalcogenide vitreous semiconductors [14] as well as in various types of polymers [15-17].

Holographically the largest possible modulation of SRG can be obtained by orthogonal -45:45 degree or circular:anti-circular polarization of the recording beams [4]. In contrast, more trivial recording conditions (p and p, p and s, s and s setups) produce a very low diffraction efficiency and small surface modulation. In the latter cases the recording efficiency can be improved by introducing an optional incoherent assisting light with a specific polarization [4]. If the right conditions are met the diffraction efficiency is more or less similar for all recording beam geometries (excluding s:p setup). Thus it is relevant to investigate this anisotropic light-induced mass transfer in finer details for a better understanding of involved physics and improvements in the production technology of optical elements.

In this paper a new kind of approach of anisotropic light induced, polarization dependent deformations in amorphous As_2S_3 is shown. In order to minimize misleading interpretations this approach excludes focused light or periodic light patterns (as it is used for holographic recording). The mass transfer dependence on the intensity and polarization of light has been investigated using a simple setup of optical slit illuminated by uniform field of light.

2. Experimental

Amorphous chalcogenide As_2S_3 films on glass with thickness of 0.5-4.0 μm were obtained by thermal evaporation and the thickness of the film was controlled in a real time by a 650nm diode laser. A single beam recording setup (shown in Fig.1.) was utilized to obtain surface modulation in the As_2S_3 samples, which were illuminated by homogenized 532 nm laser light through 10 μm wide optical slit. An optional incoherent assisting 532 nm laser source was used for softening purposes of the film thus improving the recording efficiency. Polarization of recording and assisting beams was varied by half-wave and quarter-wave plates. The obtained surface relief was mapped by atomic force microscopy (AFM) using Veeco CPII.

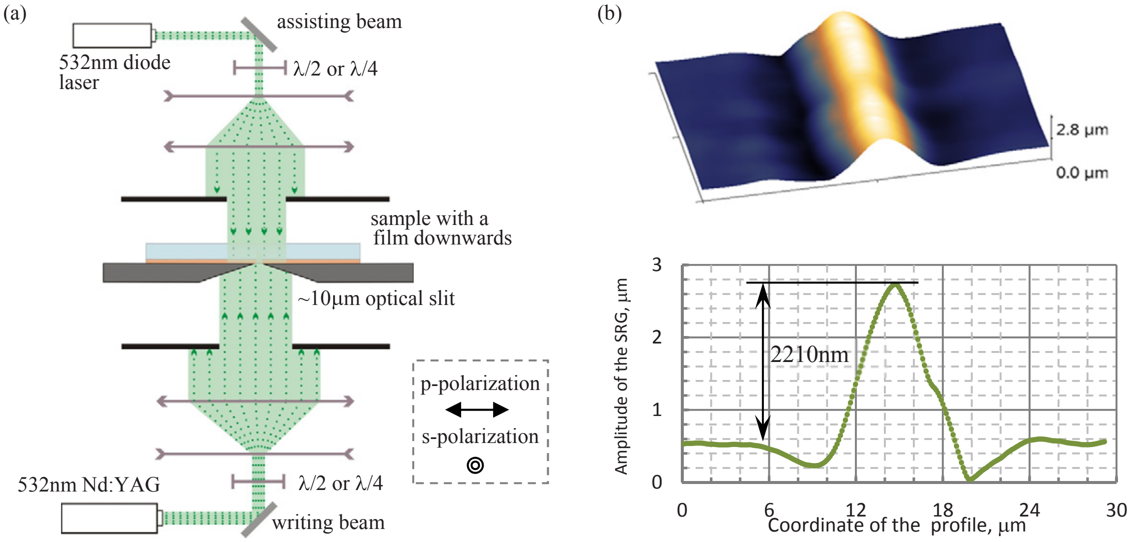

Fig.1. (a) experimental setup for formation of surface-relief structures by illumination through an adjustable optical slit; (b) 3D AFM topography picture and its profile of the 3.3μm thick As_2S_3 sample obtained by p-polarized $3W/cm^2$ illumination through optical slit and with incoherent s-polarized $1.5W/cm^2$ assisting beam (p/s setup), the length of exposure was 5h.

3. Results

If we consider various combinations of polarization in the case of holographic recording it has been determined [4] that the highest possible modulation of SRG can be achieved only in two cases – -45 and 45 degree or anti circular RCP and LCP setup. Both of these combinations stand out in the theoretical interference pattern calculations [10], their contrast is very close to zero (the intensity distribution is almost uniform). In contrary, the electric field distribution in these cases contains s and p components which are in opposite phases and the contrast for each component is 1. Since in monolayers of amorphous chalcogenides (and other certain photo-resist materials) this process is reversible [13], there is only one possibility for the lateral mass transfer: the mass moves parallel to the intensity gradient and in a opposite direction with respect to the polarization of electric field gradient. To investigate the mass transfer in these directions, a single unfocused beam recording system has been used. Unfortunately these experiments did not show any considerable mass transfer for any polarization and intensity thus an optional incoherent assisting beam with the same wavelength (532nm) was used (see recording setup in Fig.1a.) to simulate the holographic recording conditions as it is in the case of -45 and 45 degree or RCP and LCP polarization setup.

The cross-profiles of SRGs obtained in the optical slit experiments with an assisting beam are shown in Fig.1b. Due to the mass transfer a huge ridge (Δd/d=67% from the initial surface and 83% total deformation) has been obtained by the p/s setup (polarization of the writing and assisting beam are perpendicular and parallel to the slit respectively). Our opinion is that it is possible to obtain even greater

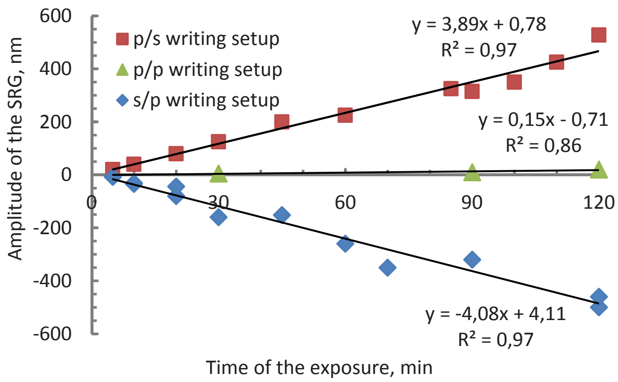

Fig. 2. Amplitude of the SRG versus time of the exposure for different polarization combinations of the writing and assisting beams (a/b symbols denote polarization for the writing and the assisting beams respectively) in optical slit experiments, intensity of the writing and assisting beam kept constant at 4.24W/cm^2 and 0.37W/cm^2 respectively

relief by longer exposure or by varying the intensity of writing and assisting beams. Therefore a major restriction for the growth of the SRG is only the thickness of photo-resist film. The minimum positions of the obtained profile (Fig.1b., 9 and 20 μm) correspond to the location of slit edges, *i.e.*, positions of high electric field gradient. It appears that in these regions the mass transfer is the most active, resulting in the formation of W-shaped profile. Thus the active region for the mass transfer was ~19μm (Fig.1b., from 5 to 24 μm) therefore there were at least 4.5 μm thick regions on both sides of the slit which were illuminated only by the assisting beam but, nevertheless, they had an impact on the process of relief formation.

To identify the influence of outside factors on the surface-relief formation, experiments with various exposure times and a wide range of intensities for the writing and assisting beam has been conducted. The time dependent formation of ridges and grooves for the 10μm wide slit are shown in Fig.2. where the experimental points are the surface profile amplitudes (from the initial surface). As can be seen, in the case of different polarization of the writing beams the direction of mass transfer is opposite. For the s polarization (s/p setup: polarization of the writing beam is parallel to the slit) the mass is transported away from the illuminated area thus forming a groove, but for the p polarization (p/s setup) this process is inverted – the mass is transported into the illuminated area thus forming a ridge. Note that the assisting beams were polarized orthogonally to the writing beams making the recording conditions similar to those for RCP and LCP or -45° and 45° holographic recording setup. The symbol a/b denotes the possible combinations of polarization, a – for the recording beam and b – for the assisting beam.

It can be seen that the formation of ridges as well as grooves in Fig.2. are strongly linear thus the data are approximated with linear trend lines. As the slope coefficients show, the gain of this surface-relief formation by orthogonally polarized assisting beam is ±4nm/min (“+” for p/s and “-” for s/p setup). After a 5h exposure the amplitude will reach 1200 nm which is a half of the amplitude obtained by 3 and 1.5W/cm^2 for the writing and assisting beams respectively (7.4nm/min, Fig.1b). Therefore, additional experiments are required to determine the optimal recording parameters for the best efficiency of direct surface-relief formation for this setup. When the polarization of the recording and assisting beams coincide (*e.g.*, p/p setup in Fig.2.), the obtained grating was with more than 25 times lower amplitude. Similar results have been obtained by s/s setup forming shallow grooves (not depicted in this work). Thus the direction of mass transfer is restricted only by the polarization of the writing beam. The relief

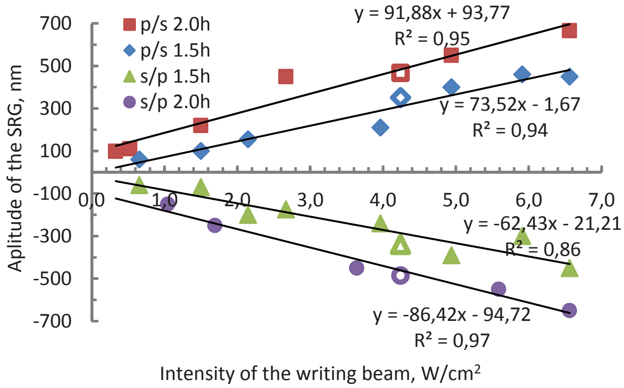

Fig.3. Amplitude of the SRG versus intensity of the writing beam for different polarization combinations of the writing and assisting beams and exposure lengths (1.5 and 2.0h) in optical slit experiments, The intensity of assisting beam kept constant at 0.37W/cm^2

formation can be substantially enhanced by an assisting beam with a specific polarization. Note that the relief obtained without assisting beam was unnoticeable for all recording parameters and exposure lengths, thus in order to investigate SRG obtained only with a single writing beam, more sensitive experiments and AFM measurements are necessary.

The obtained amplitudes of SRG's made in optical slit experiments versus intensity of the writing beam is shown in Fig.3. The intensity of assisting beam was held the same as in the experiments depicted in Fig.2.: 0.37 W/cm2 but for the intensity of writing beam was changed from 0.3 up to 6.6 W/cm^2. Despite the wide changes in the intensity of the writing beam, for all combinations of the recording setup and time of exposure the formation of surface-relief is strongly linear. The blank points which were calculated from the Fig.2. trend line equations fit well in the results for a particular recording setup. Therefore, if there is a negative thermal affect in the process of surface-relief formation, it probably manifests only at higher radiation densities. By comparing the slope coefficients for this case it can be seen that the formation of ridges is slightly more effective than the formation of grooves.

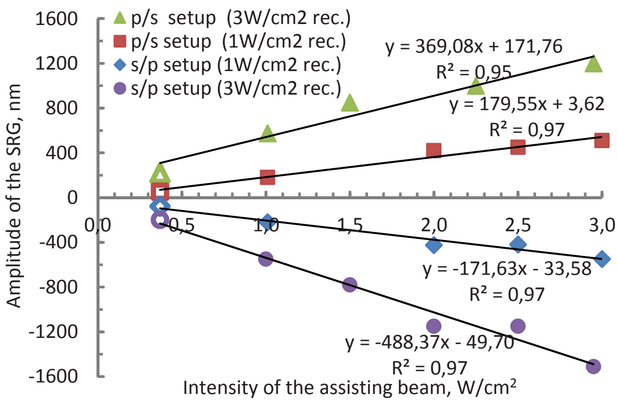

Fig.4. Amplitude of the SRG versus intensity of the assisting beam for different polarization combinations of the writing and assisting beams in optical slit experiments. The intensity of the writing beam kept at 1 and 3W/cm^2, the time of exposure 1.5h

In the previously reviewed experiments the intensity of the assisting beam was held constant and comparatively low, *i.e.*, 0.37W/cm^2. The amplitude obtained in the optical slit experiments with the assisting beam intensity varied from 0.37 up to 3W/cm^2 is shown in Fig.4. The intensity of the writing beam was 1 or 3W/cm^2 and the exposure were kept at 1.5 h. In this case the formation of surface-relief is also strongly linear for a wide range of assisting beam intensities. The blank points have been calculated from the trend line equations of Fig.3., they fit well in the extended trend lines of the corresponding recording setups. By adjusting the intensity of assisting beam it is possible to obtain comparatively greater surface-relief structures. When the intensity of writing and assisting beams are kept at 3W/cm^2 after a 1.5h long exposure it is possible to obtain roughly 1.3 micron structures. Therefore the intensity of assisting beam is not meaningless for the direct surface-relief structure patterning.

4. Conclusion

We have investigated that the light-induced mass transfer process for amorphous As_2S_3 strongly depends on the polarization of the light. The behavior of mass transfer and thus the resulting recording could be related to interaction between the polar photo-induced defects and the polarized electric field of recording and assisting illumination. It has been shown that the formation of surface relief grating in amorphous As_2S_3 films closely depends on the superposition of electric field of recording and assisting beams, thus the mass transfer can be directed both ways – towards or away from the electric field intensity gradient. The recording efficiency in an arbitrary recording setup using linearly polarized light can be significantly improved by introducing additional incoherent orthogonally polarized assisting illumination.

A direct recording technique of SRG is a comparatively new solution for lithography and, as shown in this article, provides new experimental techniques for better understanding of the interaction between the light and matter. The obtained gratings are very stable at room temperature, so this method can replace some of the chemical etching techniques and find a practical application in the applied physics.

Acknowledgements

This work has been supported by the European Regional Development Fund within the project Nr. 2010/0270/2DP/2.1.1.1.0/10/APIA/VIAA/002

References

[1] Tanaka K, Shimakawa K. *Amorphous Chalcogenide Semiconductors and Related Materials*, New York: Springer; 2011.

[2] Kryshenik VM, Trunov ML, Ivanitsky VP. Vectoral response under photo-excitation in amorphous chalcogenides and azobenzene polymer films: a comparison. *J Optoelectron Adv Mater* 2007; **9(7):** 1949–1964.

[3] Chomat M, Lezal D, Gregora I, Srb I. Relief holograms in thin films of amorphous As_2Se_3 under high laser exposures. *J Non-Cryst Solids* 1976; **20**: 427–437.

[4] Gertners U, Teteris J. Surface relief formation in amorphous chalcogenide thin films during holographic recording. *Opt Mat* 2010; **32**: 807–810.

[5] Florea C, Sanghera JS, Shaw LB, Nguyen VQ, Aggarwal ID. Surface relief gratings in AsSe glass fabricated under 800-nm laser exposure. *Mat Lett* 2007; **61**: 1271–1273.

[6] Guo Z, Qu S, Ran L, Lui S. Modulation grating achieved by two interfered femtosecond laser pulses on the surface of the silica glass. *Appl Surf Sci* 2007; **253**: 8581–8583.

[7] Hisakuni H, Tanaka K. Giant photoexpansion in As_2S_3 glass. *Appl Phys Lett* 1994; **65**: 2925.

[8] Bian S, Li L, Kumar J, Kim DY, Williams J, Tripathy SK. Single laser beam-induced surface deformation on azobenzene polymer films. *Appl Phys Lett* 1998; 7**3(13)**: 1817–1819.

[9] Ishitobi H, Tanabe M, Sekkat Z, Kawata S. The anisotropic nanomovement of azo-polymers. *Opt Express* 2007; **15(2)**: 652–659.

[10] Gertners U, Teteris J, Light intensity and its polarization relation to the photoinduced mass movement in thin layers of chalcogenide vitreous semiconductors. *J Optoelectron Adv Mater* 2011; **13(11-12)**: 1462–1466.

[11] Kokenyesi S, Ivan I, Takats V, Palinkas J, Biri S, Szabo IA. Formation of surface structures on amorphous chalcogenide films. *J Non-Cryst Solids* 2007; **353**: 1470–1473.

[12] Tanaka K, Terakado N, Saitoh A. Photoinduced anisotropic deformations in covalent chalcogenide glasses. *J Optoelectron Adv Mater* 2008; **10(1)**: 124–130.

[13] Gertners U, Teteris J. Photo-induced Mass Transfer in Chalcogenides. *IOP Conf Ser: Mater Sci Eng* 2011; **23**: 012007.

[14] Saliminia A, Galstian TV, Villeneuve A. Optical Field-Induced Mass Transport in As_2S_3 Chalcogenide Glasses. *Phys Rev Lett* 2000; **85(19)**: 4112–4115.

[15] Cojocariu C, Rochon P. Light-induced motions in azobenzenecontaining polymers. *Pure Appl Chem* 2004; **76(7–8)**: 1479–1497.

[16] Yang J, Zhang J, Liu J, Wang P, Ma H, Ming H, Li Z, Zhang Q. Holographic grating recording in azobenzene polymer films. *Opt Mat* 2004; **27**: 527–532.

[17] Mohajerani E, Nataj NH. Studying the temperature dependence of the laser induced birefringence in azo dye doped polymer films. *Opt Mat* 2007; **29**: 1408–1415.