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RESEARCH PAPER

RELIEF GRATING INDUCED BY PHOTO-EXPANSION IN Ga-Ge-S AND Ga-Ge-As-S GLASSES

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We report the fabrication of relief diffraction gratings recorded on a surface of photosensitive $Ga_{10}Ge_{25}S_{65}$ and $Ga_5Ge_{25}As_5S_{65}$ glasses by means of interference of two UV laser beams at 351 nm. The diffraction efficiency (η) of first diffraction order was measured. Atomic-force-microscope (AFM) was used to perform a 3D imaging analysis of the sample surface topography that shows the superposition of an imprinted grating over the topography of the glass. The change in the absorption edge and the refractive index has been evaluated and a structural approach of the relief grating on the glass surface has been discussed.

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1. Introdution

Chalcogenide glasses became attractive for integrated optical devices: they are transparent in the infrared region, they are chemically and mechanically robust and their optical quality is high and widely tunable. In addition, they have been the subject of systematic studies for many years because of the changes in physical and chemical properties which occurs on these samples after exposure and annealing [1-3] and because of the potential applications of these effects in areas as of sub micron lithography, holography, optical memories and imaging [4, 5]. These optical devices can be patterned in chalcogenide glasses by illumination with bandgap light, which cause photobleaching [6], and photoexpansion [7]. In our previous investigation [10] of photoinduced changes on the optical properties of glass of $Ga_{10}Ge_{25}S_{65}$, we have reported a photoexpansion associated with a photobleaching [8]. While, photobleaching is a photo-induced blue shift of the optical absorption edge, photoexpansion is an increase in the volume of a photodarkened (or photobleached, in our case) chalcogenide glass. A positive volume change was also observed in As_2S_3 or As_2Se_3 and was used to produce convex microlens [9] .The present work uses the photoexpansion effects to holographically record diffraction grating in bulk $Ga_{10}Ge_{25}S_{65}$ and $Ga_5Ge_{25}As_5S_{65}$ glasses. Depending on the power density, the diffraction efficiency of the recorded hologram can be increased from 0.24 % to about 30%. Diffraction efficiency measurements and atomic force microscopy (AFM) image of the gratings demonstrated that the photoexpansion creates a surface relief grating on the glass and is accompanied by a decrease on the refraction index in the transparent spectral range below the absorption edge. The fraction expansion ($\Delta V/V$) about 5% and diffraction efficiencies up to 30% and grating period was varied from 1 to 5 μm are observed in these glasses.

2. Experimental

Glass samples were prepared by melting of high pure starting elements (Ga, Ge, and S) in a special quartz ampoule evacuated up to 10^{-3} Pa. All procedures including synthesis, distillation and

glasses production can be carried out in closed systems. After melting at 900 ^oC during 6 hours the ampoule was removed, quenched in water and annealed at the glass transition temperature, T_g, around 400^o C. Glass rod about 60 mm in length and 10 mm in diameter was removed after cutting the quartz ampoule. Pieces of around 2 mm in thickness were cut and polished.

An Ar ion laser beam (λ_1 = 351 nm) was divided into two beams with the same intensity by a half mirror, and they were recombined on the glass surface with the same incident angle. Thus, a diffraction grating is recorded in the glass, having fringes normal to the surface. The average intensity of both recording beams was varied between 20 to 70 mW/cm^2. The 1/e^2 gaussian laser beam diameter was 0.6 mm. The readout wavelength of the grating was done with a He-Ne laser beam (632.8 nm). The recording photon energy $h\omega$=3.52 eV was greater than the optical band gap E_g = 2.66 eV. The set of gratings was made with a writing angle varying from 2^o to 20^o. For wavelengths of 351 nm, this corresponds to periods of 5 to 1 μm, respectively. The diffraction efficiency η is defined as

$$\eta(t) = I_d(t) / I_o \quad (1)$$

where $I_d(t)$ is the intensity of the first order diffracted beam.

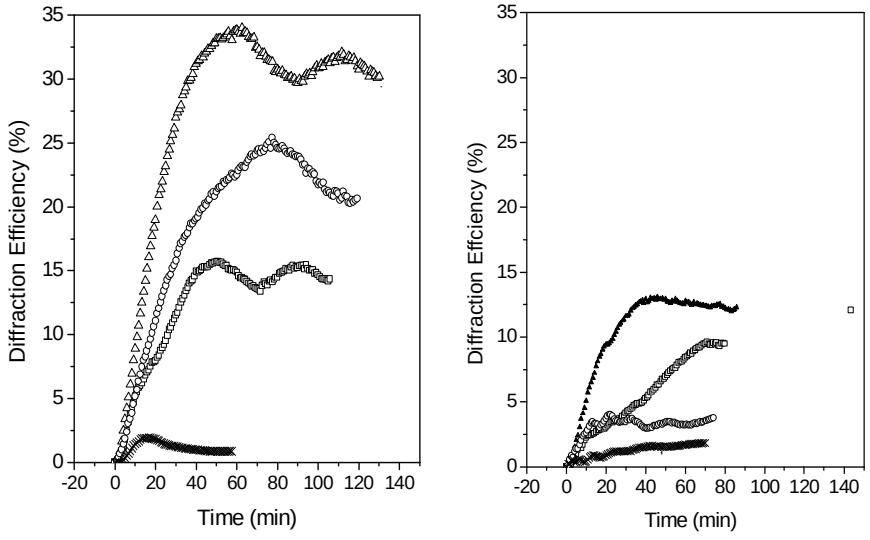

Fig. 1. The kinetics of the diffraction efficiency of relief gratings recorded in the $Ga_{10}Ge_{25}S_{65}$ (a) and $Ga_5Ge_{25}As_5S_{65}$ (b) glasses and probed with a cw He-Ne laser at 633 nm. The power density of interfering UV beams is (□) 20 mW/cm^2, (Δ) 30 mW/cm^2, (o) 50 mW/cm^2 and (x)70 mW/cm^2.

3. Results

Fig. 1 shows the kinetics of the diffraction efficiency in the samples $Ga_{10}Ge_{25}S_{65}$ (a) and $Ga_5Ge_{25}As_5S_{65}$ (b) with a writing angle of 10^o as a function of the applied power density and exposure time. The kinetics was probed with a cw He-Ne laser at 633 nm.

Bragg gratings that were fabricated varying the power density from 20 to 70 mW/cm^2 revealed an increase of diffraction efficiency reaching a maximum value for power density (I) equal to 30 mW/cm^2 after 20 minutes of exposure time implying that this dosage corresponds a saturation value. The kinetics was non-monotonous and sometimes even oscillating at lower and higher power density of interfering beams. Additional measurements of diffraction efficiency showed that the writing angle does not affect the value of the diffraction efficiency (Table 1).

Table 1. Diffraction efficiency of $Ga_{10}Ge_{25}S_{65}$ and $Ga_5Ge_{25}As_5S_{65}$ glasses at different writing angles.

	$Ga_{10}Ge_{25}S_{65}$			$Ga_5Ge_{25}As_5S_{65}$		
	$\theta = 3^o$	$\theta = 6^o$	$\theta = 10^o$	$\theta = 3^o$	$\theta = 6^o$	$\theta = 10^o$
I= 20 mW/cm^2	14.8	15.0	15.7	3.2	2.9	2.6
I= 30 mW/cm^2	34.6	34.2	33.7	10.2	11.8	13
I= 50 mW/cm^2	23.4	22.7	25.2	4.8	4.5	4.0
I= 70 mW/cm^2	1.9	2.0	1.9	1.3	1.2	1.1

The diffraction regime on phase gratings is determined [10] by the phase correlation of diffraction orders:

$$Q = \frac{2\pi\lambda d}{n_o \Lambda^2} \tag{2}$$

and by the amplitude of the phase modulation,

$$\Delta\Phi = \frac{2\pi\Delta n d}{\lambda \cos\theta} \tag{3}$$

where λ is the incident light wavelength, d is the grating thickness, n_o is the refractive index, Λ is the grating period, Δn is the modulation amplitude of the refractive index, and θ – the incident angle of the probing beam. In the Raman-Nath diffraction regime if $Q < 0.5$ and $Q\Delta\Phi < 1$ we have a "thin grating".

In our diffraction experiments, with the He-Ne reading beam and the experimental parameters, λ = 351 nm, d = 220 nm, n_0 = 2.0, Λ = 1.5 μm, one can calculate Q = 0.1 e $Q\Delta\Phi$ = 0.12. In this case the relief grating observed may be analyzed as thin gratings operating in the Raman –Nath regime.

Fig. 2 is an AFM image of a 1.2 μm period grating written with an exposure of 30 mW/cm^2. Fig. 2a shows a surface relief grating of the $Ga_{10}Ge_{25}S_{65}$ glass with excursion amplitude for this grating about 220 nm that reaches a maximum of diffraction efficiency of 35% after 20 min of exposure. Fig. 2b is a top view of of the same sample as in Fig. 2a.

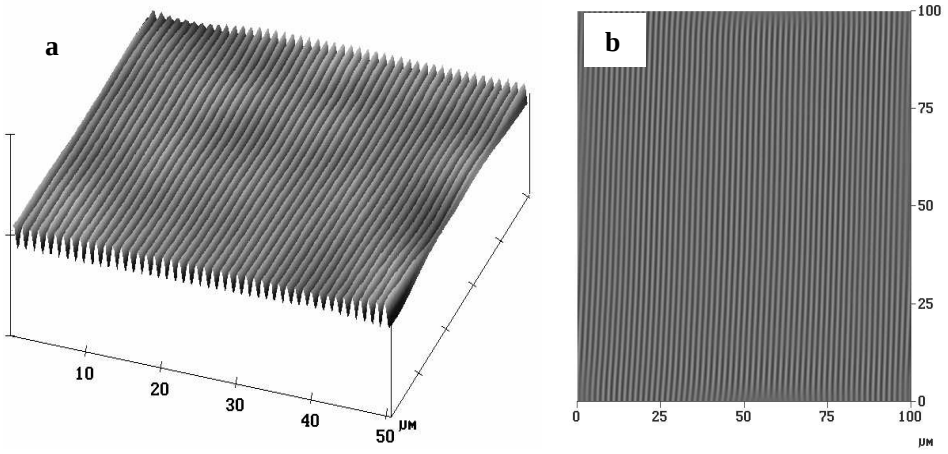

Fig. 2. Atomic force microscopy-image of the surface of the holographic grating recorded on a $Ga_{10}Ge_{25}S_{65}$ glass. The image shows a surface consisting of trenches and grooves, on which a sinusoidal grating has been "photowritten" (a) 3D profile and (b) top view.

The periods value has been also measured by optical microscopy and compared to the calculated value following the equation:

$$\Lambda = \lambda/2 \sin\theta \tag{4}$$

Where λ is the wavelength and θ is the incident angle. The calculated value is 1.1 μm, which is in good agreement with the experimental results.

We have measured metastable light-induced changes in the optical absorption edge (E_g) and refractive index that usually accompany the light-induced expansion in chalcogenides. We found a shift of the absorption edge to the shorter wavelengths after irradiation of our samples indicating a photobleaching effect. This shift increased as the exposure time increased. We have included in Table 2 some optical properties of these glass compositions before and after exposure.

Table 2. Some properties of the of the Ga-Ge-As-S and Ga-Ge-S glass compositions.

Samples	Transmitance (% at 351 nm)[a]	$\Delta\lambda$ (nm) [b]	Δn [(c)]	fractional expansion volume ($\Delta V/V$)
$Ga_{10}Ge_{25}S_{65}$	67-81	80	-0.3	5%
$Ga_5Ge_{25}As_5S_{65}$	69-64	12	-0.1	2%

[a] difference in transmittance before and after exposure
[b] light induced shift in the absorption edge
[c] difference in refraction index before and after exposure at 351 nm wavelength

4. Discussion

In both compositions we observed a power density dependence on the diffraction efficiency, in which the effect is larger in $Ga_{10}Ge_{25}S_6$ samples than $Ga_5Ge_{25}As_5S_{65}$ samples. These fact suggest that with an increase in the As in Ge-Ga-S glass, the network becomes less flexible. An addition of As results in polymerization of glass network (creation of S-As-S- chains) due to lower coordination number of As (3) as compared with Ge (4). In the other side, $Ga_yGe_xS_{65}$ compound with $x + y = 30$ is less polymerised compound amongst Ga-Ge-S glasses due to the presence of S_3-Ge-Ga-S_3 units [11].

The origin of these thin gratings sterns from a sinusoidal change in refractive index has been written at the sample surface. The surface grating is accompanied by a change in the optical properties due to a variety of non-linear optical mechanism. We observed oscillations of the transmission at large power densities similar to that which was detected on GeS_2 based glasses [12]. We found a negative change of the refractive index in the irradiated area. This indicates that the spatial modulation of the light intensity gives rise to a corresponding modulation of the electron and ionized donor densities (e.g., S^{2-} in Ga-Ge-S). The oscillations of the absorption coefficient and the respective oscillations of the refractive index can be responsible for the oscillations of the diffraction efficiency seen in Fig. 1. The value of the diffraction efficiency in Fig. 1 is determined by contributions from the space modulation of the surface relief and refractive index.

In fact, the electron diffuses so that the spatial amplitude of the electron density is diminished when compared to the spatial amplitude of the ionized donors density. This difference could explain the change in the optical properties. We may note that such changes in the refractive index are very important concerning their application. These applications are facilitated because we can control both the refractive index difference and amplitude modulation by exposure time and power density of illumination.

Finally, we have been looking to understand the origin of the surface expansion. Previous experimental data shown sulfur-rich region in the maxima of relieves [13]. This may be explained based on the chemical Ge-S bonds. We note that weakening of secondary bonds centred at sulfur atom can result in the movement of sulfur atom to the free volume, which appears in its environment in the course of the light-induced expansion of the irradiated area. Furthermore, the diffusion of sulfur into the irradiated area from the unirradiated surrounding can be a self-accelerating process since an enrichment in sulfur results in the extra secondary bonds and consequently in an accelerated light-induced expansion of the glass network

The importance of light-induced polymerization of glass network on the effect of light-induced expansion is indicated by the fact that the largest expansion was observed in the $Ga_{10}Ge_{25}S_{65}$ glass. An enrichment of this compound in sulfur (like in the ridges of photo-induced relieves) or

germanium (like in the valleys of photo-induced relieves) results in polymerization of glass network (creation of S-S-S [14] and Ge-S-Ge-S [15] chains, respectively) and suppression of the light-induced expansion.
We suggest that photoexcited sulfur atoms will diffuse with high probability into voids, which appear due to the expansion of glass network in the vicinity of low-coordinated sulfur atoms. This will result in the creation of new S-S bonds (or in other words, in a polymerisation of the glass network) in the irradiated area. Such a polymerisation explains (see, e.g. [6]) the effect of photobleaching, which accompanies a glass network expansion in the case of our glasses.

5. Conclusions

We presented experimental data on the effect: light-induced relief gratings recorded on the surface of Ga-Ge-S bulk glasses produced by an interference of two UV laser beams. This grating has peak to valley heights of 220 nm modulation amplitude. We determined from AFM image a 1.5 μm period grating with an exposure of 30 mW/cm^2.

The photo-expansion effect induced a fractional volume expansion that is responsible for the relief grating on the glass surface. The diffusion of chalcogen atoms into the irradiated area is observed and explained as due to the weakening of the bonds centred at the chalcogen atom.

There was obtained a significant change on the refractive index, which allows important applications in several domains as real time holography, optical grating and planar waveguides.

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