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Mechanism of photo induced mass transfer in amorphous chalcogenide films

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ABSTRACT

Surface relief gratings produced on a surface of amorphous chalcogenide films As₂₀Se₈₀ are flatten at room temperature under illumination by a near-bandgap polarized light ($\lambda = 650$ nm). The rates of the profiles flattening are dependent on the light intensity, polarization direction, and grating period. Two possible flattening mechanisms are selected: viscous flow and volume diffusion, and the flattening rates are calculated for both of them. From the comparison of the theory with the experiments, it is concluded that the process is controlled by anisotropic volume diffusion. The effective photo-induced diffusion coefficients, D_{xx} , along E -vector of the light polarization, obtained from the flattening kinetics are proportional to the light intensity ($D_{xx} = \beta_x I$) with $\beta_x = 2.5 \times 10^{-18} \text{ m}^4/\text{J}$. The diffusion coefficients D_{yy} along perpendicular direction are four times smaller, independently of the light intensity.

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1. Introduction

Over past several decades, chalcogenide glasses (ChG) have attracted great attention due to their diverse range of optical and electrical properties, large capacity for doping, tailorable photosensitivity, as well as due to a number of interesting phenomena, induced in ChG by light having photon energy comparable to the bandgap. Some of photo-induced (PI) phenomena in ChG, such as photodarkening, PI expansion, PI fluidity and plasticity, PI chemical diffusion and dissolution were widely studied [1–5]. The investigations were mainly stimulated by new possibilities for the development of micro-electronic, micro-optical, and planar integrated nonlinear optical devices [6,7].

One of fundamental physical phenomena used for fabrication of various micro-optical elements on a surface of ChG films, such as surface relief gratings (SRG), linear waveguides, dips and microlenses, is photo-induced mass transport, which consists in lateral redistribution of material under illumination by near-bandgap light. The driving forces of the mass transfer during surface patterning are defined by inhomogeneous distribution of chemical potentials of the film constituents caused by inhomogeneous distribution of the light intensity [8]. The kinetics of the mass transfer is very sensitive to the light polarization and intensity [9–12].

In spite of qualitative observations of PI mass transport, its mechanism remains unclear. Is it caused by enhanced PI fluidity or by PI

self-diffusion? To answer this question we studied kinetics of PI flattening of SRG under illumination by homogeneous light intensity. In these experiments driving forces are defined by Laplace pressure caused by surface curvature, whereas the kinetics is accelerated by light. By analyzing possible mechanisms of PI flattening we conclude that the main mechanism of the PI mass transport is volume self-diffusion. From experimental data on the kinetics of PI flattening under various light intensities and polarizations, we calculate effective PI diffusion coefficients in As₂₀Se₈₀ films and present quantitative results on their anisotropy.

2. Experimental

The experiments were performed on 2 μm thick As₂₀Se₈₀ films deposited on glass substrates by thermal evaporation. As₂₀Se₈₀ was selected as one of the most efficient materials for relief recording among the large number of Se- and S-based glasses [13]. SRGs with various periods from 1.5 to 7.5 μm were recorded using a 20 mW linearly polarized solid state laser operating at a wavelength of 650 nm, which is comparable with the band-gap energy, and special bi-prisms for two-beam illumination, which creates periodic intensity distribution. The experimental setup for holographic SRG fabrication was similar to that described in Refs. [12,14].

After fabrication, when the SRG amplitude h reached about 150 nm, the gratings were illuminated by a homogeneous light of the same laser with the polarization vector directed parallel or normal to the grating vector. The laser beam was deviated from the normal by 2° in the plane parallel to the grating vector. Thus, two

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polarization directions correspond to *p*- and *s*-polarizations, respectively. The light intensities varied from 0.03 to 2.5 W/cm².

In order to clear up the role of surface diffusion in the flattening kinetics, the gratings were also illuminated by polarized violet light ($\lambda = 406$ nm) with the intensity about 2 W/cm². Absorption coefficient, α , for this wavelength in our film is [15] about 10^5 cm⁻¹ and thus this light does not penetrate into the bulk of the film, exciting electron–hole pairs only in the subsurface layer of about 100 nm thick. It could accelerate surface diffusion, however could not enhance volume diffusion, like it occurred under illumination by red light.

Data on the profile flattening were obtained by in situ measurements of diffraction efficiency, ξ , which is proportional to h^2 for $h \ll \lambda$. The diffraction efficiency was measured using a violet laser beam (THOR Labs, $\lambda = 406$ nm, $P = 1$ mW) and was taken proportional to the intensity of the first diffraction peak in reflection mode. As the light detector, we used an Ocean Optics waveguide spectrometer connected to a PC.

3. Results

In Fig. 1 we show results on the flattening kinetics under homogeneous illumination by red light of various intensities. The light polarization in this experiment was parallel to the grating vector (*p*-polarization). Linear dependence on the $\ln \xi - t$ plots means that the grating amplitude, $h(t)$, exponentially decreases with the exposure time, i.e. [$h(t) \propto \exp(-\kappa t)$]. The flattening coefficient, $\kappa = \Delta \ln h / \Delta t = \Delta \ln \xi / 2\Delta t$, linearly increased with the intensity.

In Fig. 2a we compare the flattening kinetics under illumination by the same light intensity (~ 1 W/cm²) with *p* and *s* polarizations. Under illumination by *p*-polarized light, the SRG flattens much faster as compared to *s*-polarization. The κ_p/κ_s ratio is found to be 4 ± 1 , independently of the grating period and light intensity. On the other hand, the flattening coefficients depend considerably on Λ : the smaller Λ the greater is κ (Fig. 2b).

Under illumination by violet light, we did not observe any changes in the profile amplitude, independent of the light polarization and intensity.

4. Discussion

Mullins [16] calculated the kinetics of capillary flattening of sinusoidal profile on a solid surface for different mechanisms of the mass transfer (such as surface diffusion, volume diffusion, evaporation–

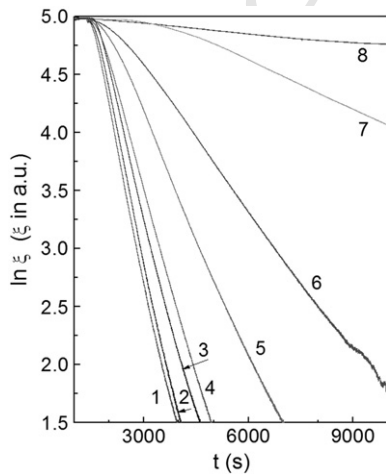


Fig. 1. Kinetics of flattening of sinusoidal profiles (period $\Lambda = 3.6$ μm) under homogeneous illumination at various intensities of light polarized parallel with the grating vector (*p*-polarization): 1–2.5 W/cm²; 2–2.2; 3–2.1; 4–1.6; 5–1.0; 6–0.7; 7–0.3; 8–0.035 W/cm².

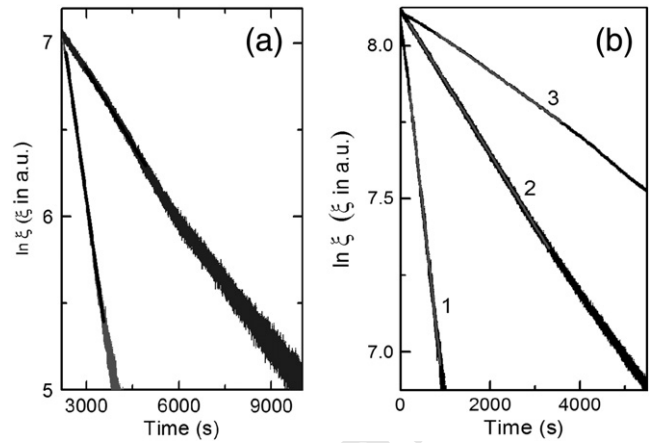


Fig. 2. Typical dependence of the flattening rates on the light polarization (a) and SRG period (b). (a) – $\Lambda = 1.5$ μm , $I = 1.03$ W/cm², 1 – *p*-polarization, 2 – *s*-polarization. (b) – 1–1.5 μm , 2–3.6 μm , 3–7.5 μm . $I = 0.35$ W/cm², *p*-polarization.

condensation, viscous flow). According to his theory, the amplitude of SRG should exponentially decrease with time, and the flattening constant, κ , depends on the mass transfer mechanism and appropriate diffusion coefficients. As seen from Fig. 1, $\ln \xi$ indeed linearly decreases with exposure time t , in agreement with the theory of capillary flattening.

In the following we neglect surface diffusion and evaporation–condensation; we did not observe any flattening under illumination by violet light, which could accelerate fast surface diffusion only. Evaporation never was observed under illumination of GhG films with intensities used in our experiments and thus we analyze two possible mechanisms: viscous flow and volume diffusion. We had to modify Mullins’ theory [16] made for surface flattening of semi-infinite solid, taking into account that the SRG period Λ and the film thickness H are comparable.

To analyze mechanism of viscous flow, we, following Mullins [16], denote by u and w the velocities parallel to x (along the surface) and z axis (towards bulk), respectively, and write the mean pressure in the form

$$p(x, z) = \gamma h q^2 e^{-qz} \sin qx. \tag{1}$$

Here, γ is the surface tension, $q = 2\pi/\Lambda$, $\zeta(x, t) = h(t) \sin qx$ describes profile of SRG. From Navier–Stokes equations (η is the viscosity)

$$\eta \nabla^2 u = \partial p / \partial x; \quad \eta \nabla^2 w = \partial p / \partial z; \quad \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0$$

with boundary conditions $u(x, H) = w(x, H) = 0$ we have found the z -component of velocity on the film surface, $w(x, 0)$, determining the flattening kinetics

$$w(x, 0) = \frac{q\gamma e^{2qH}}{2\eta} \cdot \frac{1 + 2qH - e^{2qH}}{1 + e^{4qH}} h \sin qx. \tag{2}$$

From $w(x, 0) = -\partial \zeta / \partial t$ with the initial condition $h(0) = h_0$ we obtain

$$h(t) = h_0 \exp(-\kappa_\eta t); \quad \kappa_\eta = \frac{q\gamma e^{2qH}}{2\eta} \cdot \frac{1 + 2qH - e^{2qH}}{1 + e^{4qH}}. \tag{3}$$

Eq. (3) allows estimating η from the flattening kinetics. When the film thickness exceeds the grating period ($qH = 2\pi H/\Lambda \gg 1$), the flattening constant coincides with that obtained by Mullins [16] ($\kappa_\eta = q\gamma/2\eta = \pi\gamma/\eta\Lambda$), i.e. $\kappa_\eta \propto \Lambda^{-1}$.

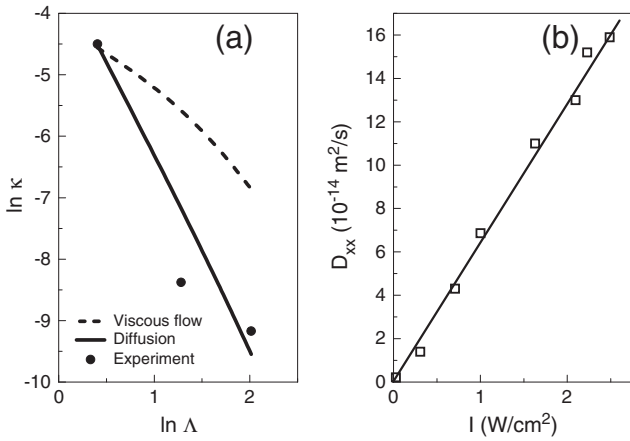


Fig. 3. (a) – Dependence $\ln \kappa$ on $\ln \Lambda$. Experimental data are compared with the theoretical dependence described by Eqs. (3) and (6) with the fitting parameters $\eta = 1$ Pa·s and $D_{xx} = 2.7 \times 10^{-14}$ m²/s for $I = 0.35$ W/cm². (b) – Dependence D_{xx} on the light intensity. $\Lambda = 3.6$ μm, p -polarization.

164 To calculate the erasing kinetics by *volume diffusion*, we use a
 165 steady state distribution of chemical potentials of pnictide (P) and
 166 chalcogene (C) atoms, $\mu_i(x, z) = p(x, z)\omega_i$, ($i = P, C$) where ω_i is the
 167 atomic volume of i -th component and $p(x, z)$ is defined by Eq. (1).

168 Diffusion fluxes are induced in both in x and z directions, with dif-
 169 ferent diffusion coefficients:

$$J_{ix}(x) = -\frac{D_{xx}^i(x)}{kT} N_i \frac{\partial \mu_i}{\partial x}; \quad J_{iz}(x) = -\frac{D_{zz}^i(x)}{kT} N_i \frac{\partial \mu_i}{\partial z}. \quad (4)$$

170 Here, $N_i(x)$ is the number of P or C atoms per unit volume of the film.
 172 With isotropic diffusion coefficients, one can neglect lateral fluxes (in x -
 173 direction) compared to normal fluxes. However, with $D_{xx}^i \gg D_{zz}^i$ (due to
 174 polarization induced diffusion anisotropy) lateral fluxes can exceed
 175 normal fluxes (in z -direction). Variation of the surface profile is

$$\frac{\partial \zeta}{\partial t} = -\int_0^H \left(\frac{\partial J_{Px}}{\partial x} \omega_P + \frac{\partial J_{Cx}}{\partial x} \omega_C \right) dz + J_{Pz}(x)\omega_P + J_{Cz}(x)\omega_C. \quad (5)$$

176 As the z -dependence of each of the fluxes is given by $\exp(-qz)$,
 179 integration by z gives a factor $[1 - \exp(-qH)]/q$, i.e. the kinetics es-
 180 sentially depends on the relationship between the film thickness H
 181 and the period Λ . Substituting Eq. (4) into Eq. (5), we obtain

$$h(t) = h_0 \exp(-\kappa_D \cdot t); \quad \kappa_D = \frac{q^3 D_{xx} \gamma \bar{\omega}}{kT} \left[(1 - e^{-qH}) + s^{-1} \right]. \quad (6)$$

182 Here, $D_{xx} = D_{xx}^P C \frac{\omega_P^2}{\bar{\omega}^2} + D_{xx}^C (1-C) \frac{\omega_C^2}{\bar{\omega}^2}$, $\bar{\omega} = \omega_P C + \omega_C (1-C)$, and $s =$
 185 D_{xx}/D_{zz} define anisotropy of diffusion coefficients in x and z -directions.
 186 The flattening coefficient, κ_D , consists of two terms. The first term de-
 187 scribes lateral diffusion flux from positive to negative parts of the pro-
 188 file; it is proportional to the diffusion coefficient in the polarization
 189 direction, D_{xx} . The second one describes diffusion flux in the perpen-
 190 dicular direction, with the diffusion coefficient $D_{zz} = D_{xx}/s$, which is
 191 several times smaller than D_{xx} . With $qH \gg 1$ κ_D becomes independent
 192 of H and proportional to Λ^{-3} , in agreement with the Mullins' theory
 193 [16].

195 Due to different dependences of the flattening coefficients, κ_η and κ_D
 196 on the grating period Λ , we can determine the main mechanism of the
 197 mass transport. Fig. 3a shows $\ln \kappa_\eta$ and $\ln \kappa_D$ vs $\ln \Lambda$ calculated using
 198 Eqs. (3) and (6), for viscous flow and diffusion mechanisms, respective-
 199 ly, in comparison with the experimental data obtained for gratings with
 200 $\Lambda = 1.5, 3.6,$ and 7.5 μm (see Fig. 3). One can see that the experimental
 201 data confirm the *volume diffusion* mechanism of flattening. The calculat-
 202 ed curve, $\ln \kappa_D$ vs $\ln \Lambda$ has a slope of -3.05 ± 0.5 , in accordance with
 203 Eq. (6). In Fig. 3a the dependence of $\ln \kappa_\eta$ on $\ln \Lambda$ (dotted curve) is also
 204 shown, calculated for viscous flow mechanism using Eq. (3) and
 205 $\eta = 1$ Pa s obtained for $\Lambda = 1.5$ μm. This curve has a slope $n \approx -1$ and
 206 thus deviates from the experimental points for $\Lambda = 3.6$ μm and
 207 $\Lambda = 7.5$ μm. Coefficient s was taken $\kappa_P/\kappa_S \approx 4$, as obtained from the
 208 experiments.

209 The diffusion coefficients D_{xx} calculated using Eq. (6) from the
 210 slopes of straight lines in Fig. 1 were found to be proportional to the
 211 light intensity ($D_{xx} = \beta_x I$) with the coefficient $\beta_x = 6 \times 10^{-18}$ m⁴/J
 212 (Fig. 3b).

213 In summary, it is shown that kinetics of photo-induced erasing of
 214 SRG in As₂₀Se₈₀ films depends on the light intensity, polarization di-
 215 rection and grating period. According to our theoretical model, the
 216 flattening occurs under capillary forces caused by local curvature of
 217 surface profile. It is concluded that the main flattening mechanism
 218 is volume diffusion and the effective diffusion coefficients along polar-
 219 ization direction, D_{xx} , can be expressed as $D_{xx} = \beta_x I$. The coefficients
 220 D_{xx} four times exceed those in perpendicular directions.

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