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Mechanism of photo induced mass transfer in amorphous chalcogenide films


Dept. of Physics, Bar-Ilan University, Ramat-Gan 52900, Israel
Dept. of Solid State Physics, University of Debrecen, H-4010 Debrecen, Hungary
Dept. of Operational Physics, University of Debrecen, H-4010 Debrecen, Hungary

Department of Solid State Physics, University of Debrecen, H-4010 Debrecen, Hungary

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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 (λ=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, Dxx along E-vector of the light polarization, obtained from the flattening kinetics are proportional to the light intensity (Dxx=fiD) with fi=2.5×10−13 m²/s. The diffusion coefficients Dyy 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 wavelength 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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⁎ Corresponding author.
E-mail address: kagany@mail.biu.ac.il (Y. Kaganovskii).

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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 (λ = 406 nm) with the intensity about 2 W/cm². Absorption coefficient, α, for this wavelength in our film is [15] about 10⁵ 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 h² for h ≪ λ. The diffraction efficiency was measured using a violet laser beam (THOR Labs, λ = 406 nm, P = 1 mW) and was taken proportionally 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 ξ–t plots means that the grating amplitude, h(t), exponentially decreases with the exposure time, i.e. \[ h(t) = h_0 \exp(-\kappa t) \]. The flattening constant, \( \kappa = \Delta \ln h/\Delta t = \Delta \ln \xi/\Delta t \), 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 \( \kappa_p/\kappa_s \) 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 \( \kappa \) (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–condensation, viscous flow). According to his theory, the amplitude of SRG should exponentially decrease with time, and the flattening constant, \( \kappa \), depends on the mass transfer mechanism and appropriate diffusion coefficients. As seen from Fig. 1, ln ξ 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 GaAs 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

\[
p(x, z) = \gamma h q^2 e^{-\nu t} \sin qx.
\]

Here, \( \gamma \) is the surface tension, \( q = 2\pi/\Lambda \) and \( \zeta(x, t) = h(t) \sin qx \) describes profile of SRG. From Navier–Stokes equations (\( \eta \) 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 \( u(x, \eta) = w(x, \eta) = 0 \) we have found the z-component of velocity on the film surface, \( w(x, 0) \), determining the flattening kinetics

\[
w(x, 0) = \frac{q \gamma e^{2\pi H}}{2\pi} \left(1 + \frac{2qH - e^{2\pi H}}{1 + e^{2\pi H}}\right) \sin qx.
\]

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

\[
h(t) = h_0 \exp\left(-\kappa_s t\right); \quad \kappa_s = \frac{q \gamma e^{2\pi H}}{2\pi} \left(1 + \frac{2qH - e^{2\pi H}}{1 + e^{2\pi H}}\right).
\]

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

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Fig. 1. Kinetics of flattening of sinusoidal profiles (period Λ = 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) Λ = 1.5 μm, I = 1.03 W/cm², \( p \)-polarization, \( s \)-polarization.

(b) Λ = 1–1.5 μm, 2–3.6 μm, 3–7.5 μm, I = 0.23 W/cm², \( p \)-polarization.
To calculate the erasing kinetics by volume diffusion, we use a steady state distribution of chemical potentials of pnictide (P) and chalcogene (C) atoms, \( \mu(x, z) = \mu(x, z) \omega_i \) (i = P, C) where \( \omega_i \) is the atomic volume of i-th component and \( \mu(x, z) \) is defined by Eq. (1).

Diffusion fluxes are induced in both in x and z directions, with different diffusion coefficients:

\[
J_x(x) = -\frac{D_{xx}(x)}{kT} N_i \frac{\partial \omega_i}{\partial x}; \quad J_z(x) = -\frac{D_{zz}(x)}{kT} N_i \frac{\partial \omega_i}{\partial z}.
\]

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

\[
\frac{\partial \xi}{\partial t} = -\int_0^h \left( \frac{D_{xx}}{kT} \frac{\partial \omega_p}{\partial x} + \frac{D_{zz}}{kT} \frac{\partial \omega_c}{\partial z} \right) dz + f_{xI}(x) \omega_p + f_c(x) \omega_c.
\]

\[
\lambda = \frac{\lambda}{2.7 \times 10^{-9}} \approx 1 \text{ Pa s} \quad \text{for} \quad \lambda = 1.5, 3.6, \text{ and } 7.5 \mu\text{m}.
\]

Due to different dependences of the flattening coefficients, \(\eta_p\) and \(\eta_q\) on the grating period \(\Lambda\), we can determine the main mechanism of the mass transport. Fig. 3a shows \(\ln \eta_q\) and \(\ln \eta_p\) vs \(\ln \Lambda\) calculated using Eqs. (3) and (6), for viscous flow and diffusion mechanisms, respectively, in comparison with the experimental data obtained for gratings with \(\Lambda = 1.5, 3.6, \text{ and } 7.5 \mu\text{m}\) (see Fig. 3). One can see that the experimental data confirm the volume diffusion mechanism of flattening. The calculated curve, \(\ln \eta_q\) vs \(\ln \Lambda\) has a slope of \(-3.05 \pm 0.5\), in accordance with Eq. (6). In Fig. 3a the dependence of \(\ln \eta_q\) on \(\ln \Lambda\) (dotted curve) is also shown, calculated for viscous flow mechanism using Eq. (3) and \(\eta = 1 \) Pa s obtained for \(\Lambda = 1.5 \mu\text{m}\). This curve has a slope \(n \approx 1\) and thus deviates from the experimental points for \(\Lambda = 3.6 \mu\text{m}\) and \(\Lambda = 7.5 \mu\text{m}\). Coefficient \(s\) was taken \(\eta_p/\eta_q \approx 4\), as obtained from the experiments.

The diffusion coefficients \(D_{xx}\) calculated using Eq. (6) from the slopes of straight lines in Fig. 1 were found to be proportional to the light intensity (\(D_{xx} \propto I\)) with the coefficient \(\beta_s = 6 \times 10^{-14} \text{ m}^2/\text{J}\) (Fig. 3b).

In summary, it is shown that kinetics of photo-induced erasing of SRG in As_{20}Se_{80} films depends on the light intensity, polarization direction and grating period. According to our theoretical model, the flattening occurs under capillary forces caused by local curvature of surface profile. It is concluded that the main flattening mechanism is volume diffusion and the effective diffusion coefficients along polarization direction, \(D_{xx}\), can be expressed as \(D_{xx} \propto I\). The coefficients \(D_{xx}\) four times exceed those in perpendicular directions.

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