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Direct surface relief formation in $As_{0.2}Se_{0.8}$ layers

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The process of light-stimulated periodic surface relief formation in $As_{0.2}Se_{0.8}$ layers was investigated by *in situ* AFM depth profiling and compared with data on diffraction efficiency η of similar holographic gratings, measured in a reflection mode. It was discovered, that the time (exposure) dependence of the surface deformation Δd has at least two components, which correspond to the stable sinusoidal relief formation up to the giant, $\Delta d/d$ >10% changes in this best composition from As-Se system. It is assumed that the surface relief formation is connected with induced volume expansion (up to 1%) as well as with a lateral mass transport. A small dynamical component of η appears when the light is switched on. Most probably it depends on the charge carrier generation and corresponding changes of the refraction index.

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1. Introduction

Besides the well known photo-induced structural transformation effects and related changes of optical parameters (absorption coefficient α, refraction index n) (see for example [1]) some peculiar effects like photo-plasticity or photo-fluidity, stimulated giant expansion or contraction, birefringence also appear when amorphous chalcogenide layer is illuminated, but up to now these are rather ambiguously correlated with composition, experimental conditions [2-6] and the proposed mechanisms are also contradictory. Nevertheless these data show on the prospects of direct, one-step recording process which can be especially useful for prototyping optical, photonic elements. During the last decade a number of papers were devoted to the investigations of surface deformations and direct recording of surface geometrical relief in different chalcogenide layers [7-8]. Usually the initial and final state of the surface, the presence of surface bumps or grooves is examined; sometimes the kinetics of recording is followed by measuring the holographic efficiency of the periodical structure, or by the interferometric measurements [9]. To our best knowledge no direct observation of the real surface transformations during holographic recording in chalcogenide glasses were performed up to now. We have done it *in situ* in the AFM and presented the results in this paper. To make the results more expressive and applicable we investigated the simplest chalcogenide glass compositions from As_xSe_{1-x} system ($0 \le x \le 0.5$) with a well known model structure and rather easy technology, which reveal almost all of the above-mentioned photo-induced effects. The most efficient composition $As_{0.2}Se_{0.8}$ which reveals giant photo-expansion and photo-plasticity effect [8] was selected for more detailed investigations.

2. Experimental

Besides a lot of advantages of arsenic selenide glasses as materials for optical recording (sensitivity in a red spectral region, absence of crystallization effects, etc.) one is very important: thin films of proper composition can be easily fabricated by thermal evaporation of corresponding bulk glasses in vacuum. A number of bulk As_xSe_{1-x} glasses (x=0.1, 0.2, 0.3, 0.4 and 0.5) were fabricated first from high purity (99.9999%) components by usual technology and powdered before evaporation. Glass plates were used as substrate for films. It was confirmed by EDAX measurements that the composition of as deposited films correspond to the initial glass. The film thickness was usually 1 or 2 μm.

The known experimental set-up for holographic recording by two coherent converging laser beams was modified for *in situ* measurements of surface deformations in AFM. The laser diode module (λ=650 nm, output power P=20 mW), the 90° beam deflector and a Fresnel biprism from Al_2O_3 were assembled in one module, which enabled us to create a periodical, close to the sinusoidal lateral distribution of intensity and polarization state of light in the chalcogenide film sample placed on the top of the device. So the recording was performed via the substrate and chalcogenide layer and the scanning of the surface by AFM tip (Digital Instruments NanoScope Dimension 3100). Each scan takes a few seconds, so the time-dependence of the grating development was monitored. We used the same module for hologram recording with red ((λ=650 nm) laser beam and optical readout in a reflection mode by a blue laser beam (THOR Labs, λ=408 nm, P=1 mW). This wavelength is far in the spectral range of the fundamental absorption of arsenic selenides ($E_g \approx$ 1.9-2.1 eV) and so only the reflection from the surface was measured. The light detector was an Ocean Optics

waveguide spectrometer connected to the PC. Hologram efficiency was taken proportional to the intensity of the first diffraction peak. All experiments were done in a normal ambient condition, at room temperatures.

3. Results

First we have recorded surface relief gratings (SRG) at the same conditions in the mentioned number of different compositions from As_xSe_{1-x} system and found that in spite of similarities the best results (the highest surface relief) were obtained in $As_{0.2}Se_{0.8}$ films. It was in accordance with our previous result on measuring surface deformations [8]. The pure Se layers were also investigated but there was a danger of crystallization during the long illumination, so the more detailed investigations were performed on $As_{0.2}Se_{0.8}$ composition.

In situ AFM measurements of the surface profile development showed nice sinusoidal relief (Fig.1 and Fig.2.), which increased with exposition completely similarly to the η (Fig.2.b.). The grating period was 2.5 μm so the groove aspect ratio $\Delta d/\Lambda$ (profile depth/grating period) was near 0.1 at the beginning of the saturation region.

The time (exposition) dependence of the SRG efficiency contains two distinct parts, as it is presented in Fig.2.a. The first part is a fast (few seconds) but comparatively small increase of η , which is followed either by a steady state and later almost linearly increase of η, or by a simple, very long and quasi linear increase up to the saturation. The saturation usually is followed by slow decrease of η, but it is not possible to continue very long time holographic measurements to see the full dependence of the efficiency on the modulation depth.

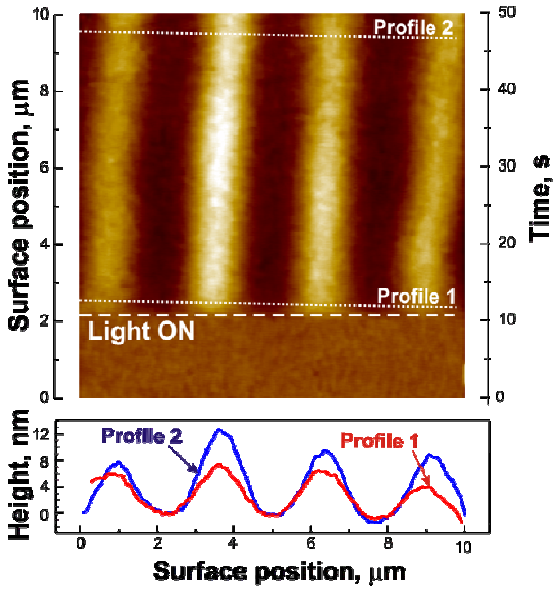

Fig. 1. In situ measurement of the surface grating formation induced by two p-polarized interfering laser beams in a 2-μm-thick $As_{20}Se_{80}$ film. High profiles at 2 and 35 s of exposure are plotted.

It was established, that the surface relief height was increasing up to 10-14 nm at the first fast stage (see Fig.3) and to the giant volumes of 300 nm or even more on a second stage in a 2 μm thick film. It means that local expansions occur up to 0.5-1.0% and 15% respectively.

Since the stability of the recorded relief is of essential interest, we checked the dynamics of the relief height and holographic efficiency when the laser light was switched on or off. Two different behaviours were discovered: at the beginning of stable increase of the relief depth and at the end or saturation of this component. Good correlation between the change of Δd and η was found again: the dynamical "jump" of Δd and η equals to few percents of the actual value and it disappears after the stabilization of the fast-recorded part of the relief. Another small dynamical component appears and works continuously at the saturation stage of the second expansion component (see. Fig. 2.b)

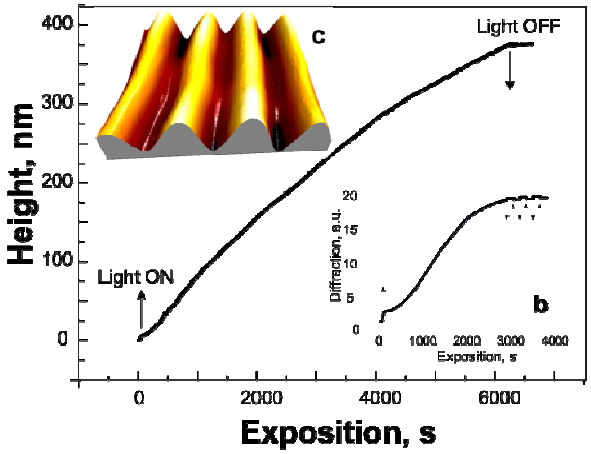

Fig.2. In situ measurements of kinetics of SRG formation on fresh 2 μm-thick $As_{20}Se_{80}$ film. In the inserts: (b) exposition dependence of the diffraction efficiency; (c) the 3-d AFM image of a typical SRG recorded on this film exposed at 6000 s.

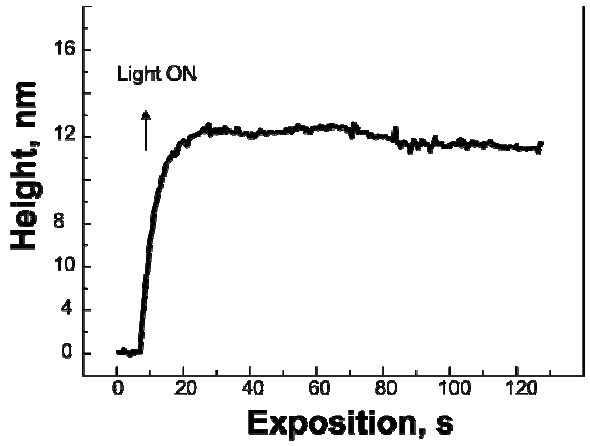

Fig.3 Initial part of the height growth under exposure time of the photoinduced SRG.

In whole the recorded reliefs are stable in a normal ambient condition for a long time (more than one year in our experiments).

4. Discussion

The relief gratings had excursion amplitudes up to 100-150 nm and thus (according to the value Q≈0.2 of the Klein factor $Q=2\pi\lambda d/n\Lambda$, where the period Λ=2.5μm is large in comparison with the modulation depth d) could be analyzed as thin grating operated in a Raman-Nath regime [10]. The depth dependence of the first order efficiency of diffraction in this case should be described as:

$$\eta = J_1^2(2\gamma), \quad (1)$$

where J_1 is the first order Bessel′s function, and γ is a grating parameter:

$$\gamma = \frac{\pi\Delta n\Delta d}{\lambda cos\theta}, \quad (2)$$

where d is the height of the surface relief profile, θ is the Bragg angle of incidence of the probe beam. For the reflection diffraction efficiency the n is the index of refraction of the air. Values for d were obtained from the AFM scans. The theoretically expected diffraction efficiencies were calculated from (1). Since the photo-induced changes of optical transmission and n in $As_{0.2}Se_{0.8}$ are the smallest in this system we took into account only the influence of Δd on η and found good correlations only at the beginning of the $\eta=f(E,t)$ dependence, up to Δd =150-200 nm. The maximum efficiency at the saturation stage corresponds to the modulation depth near 300 nm and is stable for a longer exposition times in spite of the further Δd increase to the some extent. Such a behavior shows on the necessity of some more complex analysis of these SRG, including the change of the n and polarization effects.

The mechanism of the first (fast), but rather small component of the stable η can be connected with a reversible (it can be erased by annealing at T_g) photo-induced expansion, which is known to be as large as 0.5-1.0% of the total thickness d of the layer (10-20 nm in our case). It occurs most probably due to the shift of the adjacent chain-layer like structure fragments of the glass [4,11] which accompany the bond braking and rearrangement under the light excitation.

The second, giant component of photo-induced expansion is superimposed on the first one and depends most evidently on the lateral mass transport, like it was proposed by some authors [7,12]. The background of this mechanism should be the effect of light induced fluidity or photo-plasticity as it is called in a number of papers [2,5,13,14]. In this condition the driving force (lateral gradient of the light intensity and so of the free space for diffusion of atoms or even molecules and clusters on the surface and in the bulk as well) causes the pile up of the material in the illuminated regions. It should be mentioned here that this fact is just the opposite to the situation in azobenzenes, where the diffusion of excited molecules to the dark regions is dominant [15]. The redistribution and trapping of more and less mobile non-equilibrium charge carriers (holes and electrons respectively in our materials) also can add to the driving force and so to the efficiency of this type of surface relief recording.

The dynamical component, which follow the light modulation at a sub-second time scale, can be related to the generation of free carriers , which usually causes the decrease of the refractive index of semiconductors, used, for example, for waveguide fabrication [16]. The n is usually decreasing with increasing charge carrier concentration:

$$n_0 - n = Ne^2/2n\varepsilon m^*\omega^2, \quad (3)$$

where n is the index of refraction when N non-equilibrium carriers appear, m^* is the effective mass of the carriers, ω-the plasmon frequency. These parameters are rather indefinite in chalcogenide glasses, but the change of carriers' concentration can be more as one order of magnitude, according to the measurements of photoconductivity.

Further investigations of the presented components of the relief formation, especially of the dynamical ones and the influence of the light polarization are in process and will give us a deeper insight to the complex mechanism of relief recording.

5. Summary

It is shown *in situ* and in a real time scale that the hologram recording in As-Se glasses is always accompanied by surface deformations and these have at least two components, which can dominate in compositions where the changes of the refraction index and/or transmission are not essential. The compositions near $As_{0.2}Se_{0.8}$ are the best for such a surface relief recording and can be used for prototyping optical elements, integrated optical structures.

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