Functional Materials 6, No.3 (1999)

Surface relief formation at hologram recording in a–Se/As_2S_3 nanolayered films

A.Kikineshi, V.Palyok, A.Mishak, I.Szabo, D.L.Beke**

Department of Solid-State Electronics, Uzhgorod State University,
46 Pidhirna St., Uzhgorod, 294000, Ukraine
*Department of Solid State Physics, L.Kossuth University,
H-4010 Debrecen, P.O. Box 2, Hungary

Holographic diffraction gratings (HDG) recording in the nanolayered, periodically modulated films of a–Se and As_2S_3 is investigated. The essential role of surface deformation (expansion up to 4–5 % in illuminated regions) at real time-scale hologram recording in such structures is established. The surface relief and diffraction efficiency dependencies on the recording conditions are examined and compared with a surface relief formation by selective chemical etching of the exposed single chalcogenide glass layer. The possible effects of mutually additive or exclusive components of light modulation in reflection or transmission measurement modes are analyzed.

Исследованы голографические дифракционные решетки, записанные в наносло истых периодически модулированных пленках a–Se и As_2S_3. В даных структурах установлена существенная роль поверхностной деформации (расширение вплоть до 4–5 % в облученных областях) при записи голограмм в реальном масштабе времени. Исследованы зависимости поверхностного рельефа и дифракционной эффективности от условий записи. Проведено сравнение с образованием поверхностного рельефа путем селективного химического травления облученного однородного слоя халькогенидного стекла. Проанализированы возможные эффекты взаимно аддитивных или исключающих компонентов модуляции света при измерениях в режиме отражения или пропускания.

1. Introduction

Photostructural transformations (PST) of the chalcogenide vitreous semiconductors (ChVS) are well known and widely used for amplitude-phase optical recording due to the direct connections between the PST and the change of optical parameters (coefficients of transmission τ and reflection R, refraction index n) [1–4]. PST are divided into two main types — reversible and irreversible. Reversible PST allows successive cycles of illumination (recording at room temperature) and erasing the optical relief of $\Delta\tau$, Δn, ΔR by annealing of the sensitive material below its softening temperature T_g (T_g = 305 K for a–Se, 380–450 K for a number of As–S(Se) based ChVS). Reversible PST are connected with small deviations in the metastable structure of the ChVS layer [4]. Irreversible photo- and thermoinduced processes are usually observed in as-deposited ChVS layers. These are connected with the transition of the initially metastable, defect glass structure towards the more stable one or towards the crystalline state what may be accompanied by volume (thickness d) contraction [5] or expansion [6], usually within ≈ 0.5 %. Giant photocontraction effect in obliquely deposited Ge–Se films (up to $\Delta d/d \approx 10$ %) [7] was attributed to the intrinsic transformation of the columnar structure or the decomposition processes at elevated temperatures.

Small surface relief formation at hologram recording with an intensive laser beams was supposed for As_2Se_3 homogene-

ous thick layer [8]. Since the surface relief formation is important for the fabrication of holographic optical elements, moulds for printing, the photo-resist processes were developed due to the selective chemical etching of the exposed ChVS film [2, 9] or Ag-ChVS double layer [10]. The disadvantage of this process is the additional step of wet etching in alkaline, amine or other solutions and the possible additional noises, distortions due to the surface defects, nonlinearity of etching in the nonuniformely exposed, optically absorbing layer.

Optical recording processes may be tailored by the glass composition and technology conditions of the layer deposition [4]. Artificial nanostructures [11, 12] suggest new possibilities to operate PST in ChVS layers and to use them for optical recording. These possibilities are connected with size-determined optical effects, change of the thermodynamic parameters and possible interdiffusion and stress in nanolayered structures, which may enhance also volume expansion or contraction. Large volume expansion was first time observed at hologram recording in a–Se/As_2S_3 nanolayered structure and used for one-step HDG-fabrication.

2. Experimental methods and objects

Periodical multilayered nanostructures (MNS) containing 5 to 20 nm thick alternating pairs of a–Se/As_2S_3 layers with a total thickness d of the structure up to 0.5–2.5 μm were investigated. Comparison was made with single AsSe layers with the same total thickness. The MNS samples were obtained in repeated cycles of thermal evaporation of initial glasses in vacuum and successive deposition of sublayers onto Corning 7059 glass, Si-wafer or transparent crystal surfaces. Periodicity was controlled by Small Angle X-ray Diffraction (SAXD) method. Few cross sections of MNS were investigated by Transmission Electron Microscope (TEM). The comparison of SAXD and TEM results with a surface geometry analysis made with Atomic Force Microscope (AFM) showed rather smooth interfaces and surfaces in as-deposited samples with roughness not exceeding 0.8 nm (see Fig.1,b). Surface hologram reliefs were investigated with the same AFM.

Holographic gratings with a period $\Lambda = 1$ μm were recorded with a He-Ne laser ($\lambda = 0.63$ μm with output capacity density

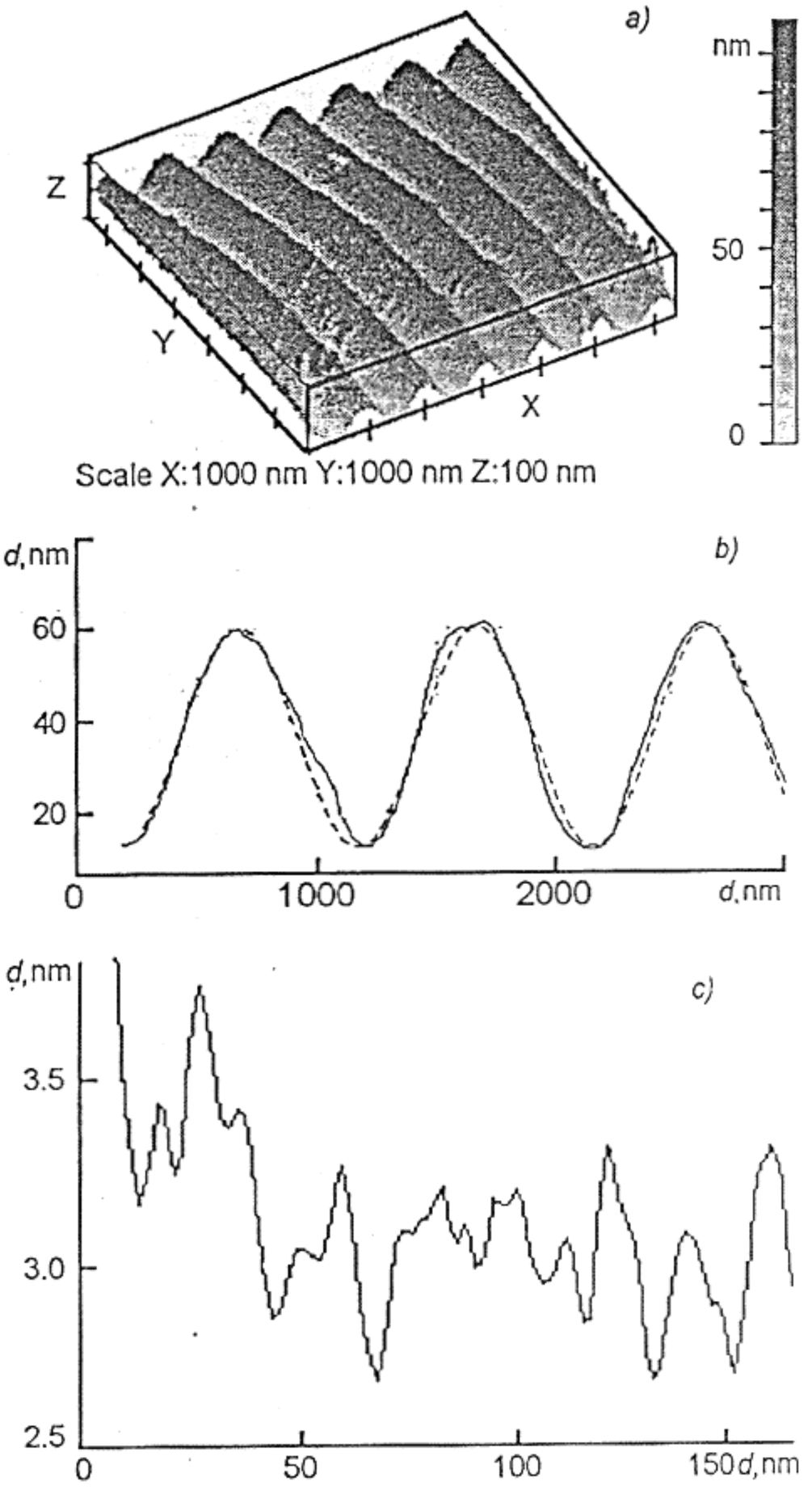

Fig.1. a) AFM picture of the surface relief hologram in F2a–Se/As_2S_3 multilayer. b) Surface relief profile and calculated sinusoidal fitting curve for the same multilayer. c) Surface roughness of the exposed layer.

$P = 0.8$ W/cm^2) in a lenseless Fourier holography mode, in a normal atmosphere.

Since the "barrier" layers (As_2S_3) with large optical bandgap $E_g^* \cong 2.5$ eV are transparent at $\lambda = 0.63$ μm and are less sensitive than the "well" layers (a–Se), $E_g^* \cong 1.9$ eV, the letter are optically excited by the laser light and PST first of all occurs in these sublayers. Samples were heated and/or annealed *in situ* during the optical measurements or treated in a separate heated chamber with normal atmosphere.

3. Results and discussion

Hologram may be recorded due to the τ, R and n and optical path changes in the recording medium. So it is an efficient

method of PST investigation, besides applied importance for the HDG and other optical elements fabrication [2, 10]. Our experimental conditions correspond to thin holograms and to the write-readout at the same wavelength.

The maximum diffraction efficiency η in transmission mode at $\lambda = 0.63$ μm obtained after $E \approx 50$ J·cm^{-2} exposure was usually 1–3 % in homogeneous AsSe layer, which is one of the best among the known ChVS. In homogeneous a–Se layer it was much smaller: $\eta \leq 0.1$ %. The η values measured in reflection mode were also small. The large self-absorption decreases the η of the absorption hologram ($\alpha = 10^3$ cm^{-1} at $\lambda = 0.63$ μm, so the maximum possible $\eta = 6.25$ % for thin absorption hologram can not be achieved). The photo-bleaching process in some cases results in higher η values [4]. Let us analyze the case of AsSe homogeneous layer before analyzing a–Se/As_2S_3 results.

It is in accordance with theoretical predictions [3]: if only amplitude is taken into account,

$$\eta = \frac{t_0^2 m^2}{4}, \qquad (1)$$

where $m = (t_{max} - t_{min})/2t_0$ is the factor of transmission amplitude modulation and $t_0 = (t_{max} + t_{min})/2$. For our case of τ change for 10 % the calculated $\eta \cong 0.023$ %. The calculated η for simple reflection hologram with ΔR change corresponding even to the relatively large photoinduced refraction index change $\Delta n = 0.04$ in layer plane gives us $\eta \cong 0.03$ % for AsSe layer.

More effective should be the phase hologram, due to the $\Delta n \cong 0.04$ in AsSe at PST [1, 3, 4], but η is restricted by the above mentioned self-absorption for *in situ* real-time scale measurements in transmission mode. For the first order reconstruction in the case of thin phase hologram:

$$\eta = k^2 J_1^2 \left(\frac{2\pi \Delta n d}{\lambda \cos\theta} \right), \qquad (2)$$

where k — the amplitude transmission, J_1 — first order Bessel function, d — the layer thickness, θ — the angle between recording beams, λ — the free space wavelength. In this case, supposing 100 % transmission, the calculated η value not exceeds 1–3 % for the investigated homogeneous 1 μm thick AsSe layer, in good accordance with experiment, where $\eta = 3.1$ %.

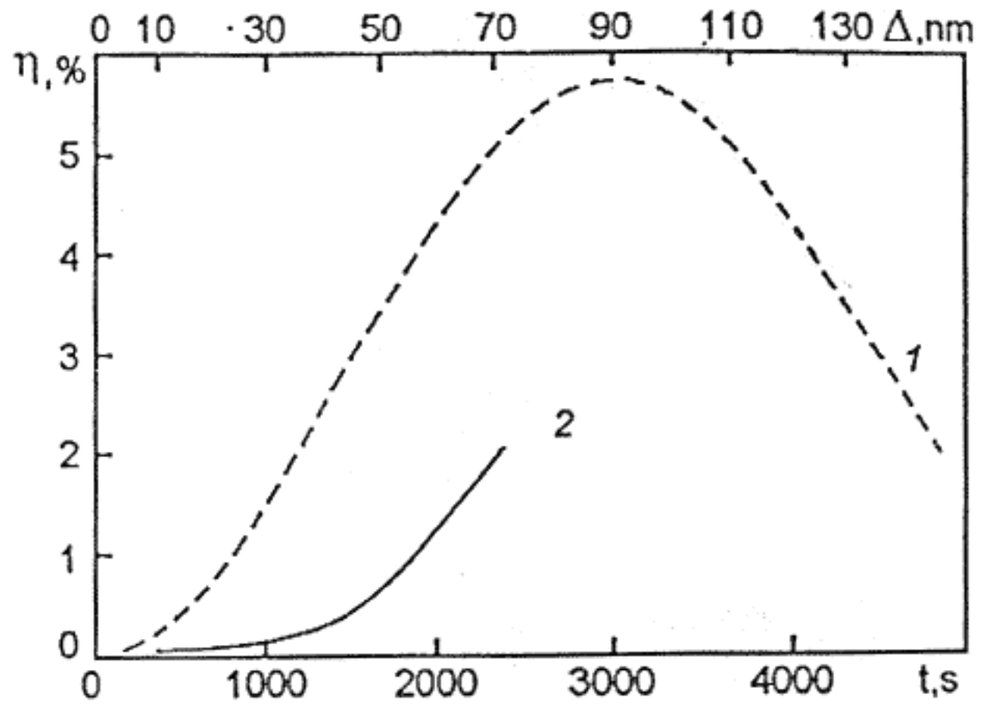

Fig.2.(1) Calculated dependence of η on modulation depth Δ for the real case of ChVS surface deformation. (2) Experimental dependence of the diffraction efficiency on exposition.

It seems that the most effective in our case may be the change of the layer thickness and surface relief formation. Really these were observed for the first time here in the case of direct real time-scale recording in MNS of chalcogenide glasses (see Fig.1). We know only one paper of M.Chomat et al.[8], where the much smaller surface relief formation was supposed at hologram recording in As_2Se_3 homogeneous layers under high laser exposures.

The surface relief hologram gives:

$$\eta = k^2 J_1^2 (4\pi\Delta/\lambda), \qquad (3)$$

where Δ is the deformation excursion [14].

Maximum value of η may be 33.9 %, but usually it is smaller because of the losses, first of all small reflection values. The experimental results of the hologram recording on a–Se/As_2S_3 MNS are in good accordance with the calculated dependencies (see Fig.2): the measured $\eta = 3.5$ % at the saturation state corresponds to the calculated 50 nm deformation excursion with the correction of the R to the real value instead of 100 %. This η value is in a good accordance with the surface profile depth, measured with AFM and presented in the Fig.1.b.

Interference pattern in the layer plane during HDG recording has a sinusoidal intensity distribution. The relief depth distribution (Fig.1.b) correlates well with the intensity distribution:

$$I = I_0/2\,(1 + \cos(2\pi x/\Lambda)), \qquad (4)$$

where I_0 is the intensity in the maximum, Λ is the interference pattern period. So the changes of the layer structure upon illumination are almost linear, until the saturation is reached.

Analyzing the kinetics of the relief and η growth on the exposure E (or irradiation time t for the given intensity capacity P), in comparison with theoretical one (Fig.2), it is evident, that our experimental results correspond to the initial part of this dependence, and the maximum efficiency may be reached only on ~4 μm thick structure, supposing the maximum 5 % thickness expansion, as it was established for this type of lightsensitive media. The saturation in our case is connected with the maximum PST. The following noise growth, smoothening of the grating causes the η decrease during hologram recording. The reached efficiency and surface profile are stable at room temperatures, but η relaxation occurs with exponentially decreasing elaxation times versus increasing temperatures and with activation energies in 30–70 kJ/mol range, which are similar to the measured values in homogeneous layers [4, 12] and usually are observed as β-type structural relaxation processes in glasses [15].

In spite of the similarity of η and corresponding structure relaxation in AsSe, a–Se and MNS, the measured surface deformation in AsSe or AsSe/As_2S_3 does not exceeds few nanometers, corresponding to the known ≤ 0.5 % values of photodeformation in ChVS layers [5, 13]. The second difference is connected with optical transmission change: photobleaching occurs in our samples. The process is thermally enhan ced, and the deformation rate (η growth on exposure) increases with temperature until the erasing (relaxation) does not prevail. The built-in stress as well as interdiffusion can play a role in the surface relief formation, and the giant photodeformation is obviously connected with a–Se/As_2S_3 MNS characteristics. The whole picture is complex possibly with a several interconnected effects, which are not properly described theoretically for amorphous materials up to now. Our continuing experiments are pointed towards the establishment of the stress and strains role in the process of optical recording in these nanolayered structures.

The importance of such real-time recording is evident for the fabrication of surface

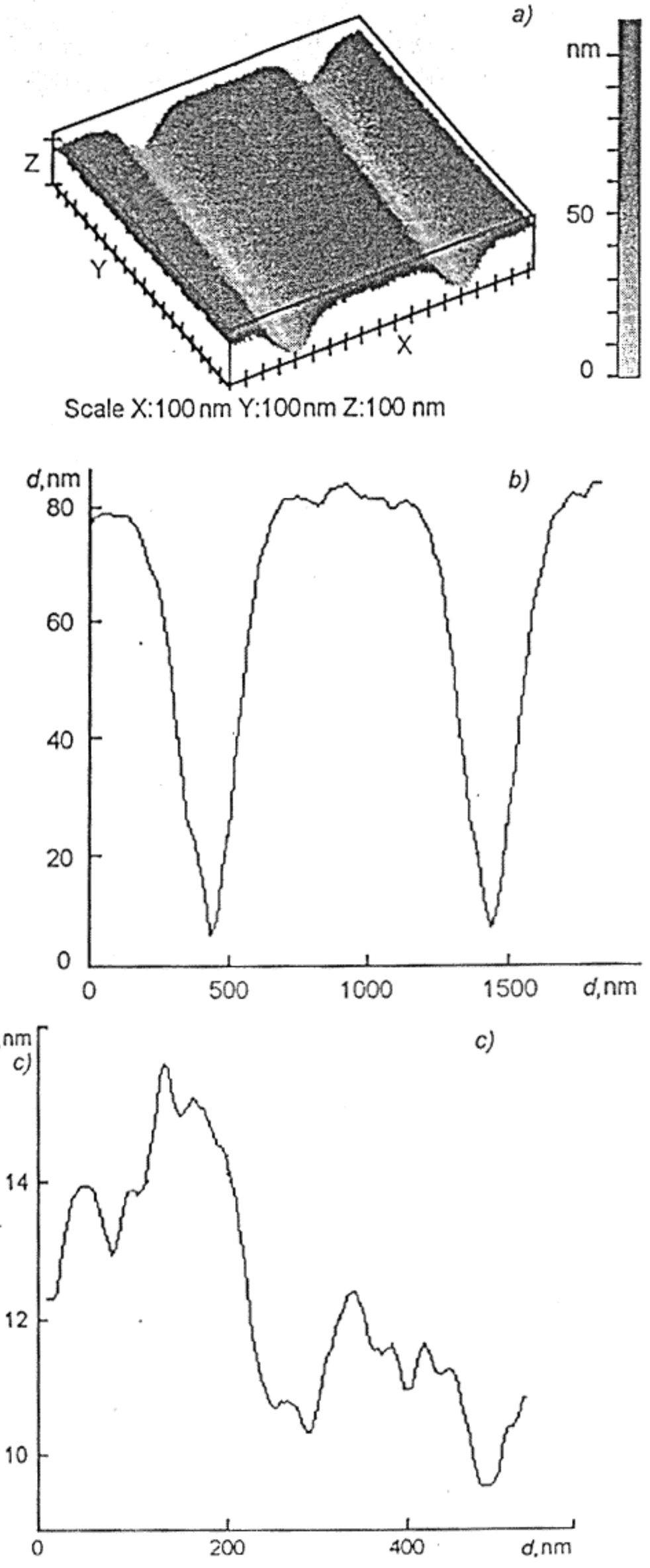

Fig.3. a) AFM picture of the recorded hologram after etching the AsSe surface. b) Surface relief profile, measured with AFM. c) Surface roughness of the etched hologram.

optical elements. The advantages consist in the real time-scale process, linearity and better quality in comparison with the etching process. The groove profile can be easily distorted during the etching of the non-uniformly exposed layer because of the rather small differences of etching rates [2] in exposed and unexposed regions, as it is dem-

onstrated for AsSe layer in Fig.3. Additional noises appear due to the surface defects formation during the etching: the roughness of the etched AsSe surface is 2–4 nm. The roughness of the exposed a–Se/As_2S_3 MNS surface as well as the initial one is not worse as 0.5–0.8 nm. The surface holograms obtained in a–Se/As_2S_3 MNS can be further processed by adding reflecting metal coatings, producing metal moulds.

4. Conclusions

The giant photoexpansion up to 4–5 % of the initial thickness was first investigated in a–Se/As_2S_3 nanolayered structures and used for hologram recording. The surface relief formation has an essential influence on the diffraction efficiency of the holographic grating recorded in the real time-scale. It was found in good accordance with the theoretical calculations for sinusoidal surface relief. The process has advantages in comparison with etching process due to the best surface quality and linearity of the recording.

Acknowledgements

The authors are indebted to Dr.M.Shipljak for his help in samples fabrication.

This work has been supported by the grant of the Ministry of Education of Ukraine as well as grant of the Ministry of Ukraine on Science and Technology 2/1345-97 and by the grant of the Hungarian Ministry of Education FKFP 0453/1997.

References

1. Ke.Tanaka, *Reviews of Solid State Science*, **4**, 641 (1990).
2. Nonsilver Photographic Processes, Ed. by A.L.Kartuzhansky, Chimia, Leningrad (1984) [in Russian].
3. K.Svarts: Physics of Optical Recording in Dielectrics and Semiconductors, Zinatne, Riga (1986) [in Russian].
4. A.Kikineshi, *Optical Memory and Neural Networks*, **4**, 177 (1995).
5. S.R.Elliott, *J. Non-Cryst. Sol.*, **81**, 71 (1986).
6. K.Shimakawa, N.Yoshida, A.Ganjoo, Y.Kuzukawa, *Phil. Mag. Letters*, **77**, 153 (1998).
7. A.Kumar, L.K.Malhotra, K.L.Chopra, *Sol. St. Commun.*, **66**, 257 (1988).
8. M.Chomat, D.Lezal, I.Gregora, I.Srb, *J. Non-Cryst. Sol.*, **20**, 427 (1976).
9. I.I.Turjanitsa, D.G.Semak, L.R.Chabibulina, *Zh. Nauchnoj i Prikladnoj Fotografii i Kinematografii*, **25**, 440 (1980).
10. I.Z.Indutnij, M.T.Kostishin, P.F.Romanenko, A.V.Stronskij, *J. Inf. Res. Mater.*, **19**, 239 (1991).
11. A.Kikineshi, *Opt. Engineering*, **34**, 1040 (1995).
12. A.Kikineshi, A.Mishak, Physics and Applications of Non-Crystalline Semiconductors in Optoelectronics, NATO ASI Series 3, High Technology, **36**, 249 (1997).
13. C.H.Dietrich, ibid, **36**, 93 (1997).
14. J.C.Urbach, R.W.Meier, *Appl. Optics*, 8, 2269 (1969).
15. D.S.Sanditov, G.M.Bartenev, Physical Properties of Disordered Structures, Nauka, Novosibirsk (1982) [in Russian].

Формування поверхневого рельєфу при голографічному запису в наношаруватих плівках a–Se/As_2S_3

О. Кикинеші, В.Пальок, О. Мишак, І.Сцабо, Д.Л.Беке

Досліджені голографічні дифракційні гратки, що записані в наношаруватих періодично модульованих плівках a–Se та As_2S_3. В даних структурах встановлено істотну роль поверхневої деформації (розширення аж до 4–5 % в опромінених областях) при запису голограм в реальному масштабі часу. Досліджені залежності поверхневого рельєфу і дифракційної ефективності від умов запису. Проведено порівняння з утворенням поверхневого рельєфу шляхом селективного хімічного травлення опроміненого однорідного шару халькогенідного скла. Проаналізовано можливі ефекти взаємно адитивних або виключних компонентів модуляції світла при вимірюваннях в режимі відбивання або пропускання.