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Journal of Non-Crystalline Solids 326&327 (2003) 515–518

JOURNAL OF  
NON-CRYSTALLINE SOLIDS

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# Selective etching of chalcogenides and its application for fabrication of diffractive optical elements

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## Abstract

Bulk samples of As and Ge based chalcogenides were synthesized from high purity elements, and thin layers (thickness  $d \approx 100\text{--}5000$  nm) were deposited by vacuum thermal evaporation and/or spin coating. Photoinduced structural changes were studied by Raman and IR spectroscopy. The kinetics of dissolution of thin layers in aqueous and non-aqueous alkaline solvents were studied. Both, positive and negative selective etching behaviours were found and used for production of diffractive optical elements (DOEs). Exposure with a halogen lamp through a Cr mask, classical holographical exposure using an Ar<sup>+</sup> laser, and direct writing laser lithography using a He–Cd laser were used to produce amplitude/phase DOEs with feature sizes of 0.37–4  $\mu\text{m}$ . Prepared low efficiency and low lifetime amplitude/phase type DOEs were transformed into corrugated relief type phase DOEs by subsequent selective etching. Positive and/or negative copies of the pattern were obtained depending on the thin layer composition, its prehistory and the applied etching bath. The profiles of the structures produced by etching were subsequently investigated using AFM and REM techniques and basic performance parameters of formed DOE were measured and compared with theoretically calculated values.

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PACS: 42.79.D; 77.84.B; 81.65.C; 78.30

## 1. Introduction

The exposure of thin amorphous chalcogenide layers to light of suitable wavelength and intensity can result in significant structural changes and thus many of their physicochemical properties are changed [1,2]. One of the most interesting proper-

ties of amorphous chalcogenide thin layers, which is changed by exposure, is their chemical resistance to alkaline solvents [2]. This phenomenon, together with extremely high-resolution capability and high transmission in VIS and IR region enables them to be applied as a medium for the production DOEs as gratings, lenses, filters, beam couplers and/or beam combiners etc. operating in broad spectral region [3]. These DOE may have advantages over conventional refractive/reflective components as regards weight, cost and ease of manufacture, and offer some new optical functionality.

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## 2. Experimental

Bulk samples of As–S, As–Se, Ge–S, As–Ge–S systems have been prepared by melting high purity (5 N) elements in evacuated quartz ampoules for 8 h at temperatures 650–700 °C (As based glasses) or 1000 °C (Ge based glasses). After synthesis, the ampoules were quenched in cold water. Thin films with thickness from 100 to 5000 nm were prepared by the thermal evaporation method (starting pressure  $1 \times 10^{-3}$  Pa) from the resistance-heated silica crucible onto microscopic slides or Corning 7059 glass slides. The deposition rate of thin layers (measured by the dynamical weighting method using a SV-1843 A Miki-FFV system) was about 1 nm/s only. Spin coating method was successfully applied as well for deposition of As–S thin layers ( $d = 100\text{--}800$  nm). In this case thin layers were heated up in inert atmosphere to 90 °C for 30 min to remove residua of applied diluent and thus to increase their stability. Final thickness was measured using the mechanical profilometer Tencor P2 and controlled by the atomic force microscopy (AFM) investigations. To minimize the extent of photoinduced effects produced by the ambient lighting, only low-level red illumination was used in the laboratory during the preparation and measurements. Photoinduced structural changes were studied by Raman and IR spectroscopy (Bruker IFS 55 IR spectrometer with FRA 106 accessory) to clarify the mechanisms of the selective etching.

Exposure with halogen lamp through Cr mask, classical holographical exposure ( $\text{Ar}^+$  laser at  $\lambda = 514$  nm, Coherent Innova model 304) and direct writing laser lithography using a He–Cd laser at  $\lambda = 441$  nm (DWL66, Heidelberg Instruments Mikrotechnik GmbH) were used to produce amplitude type DOEs with feature sizes of 0.37–4  $\mu\text{m}$ . These amplitude type DOEs were transformed into relief type DOEs (gratings, crossed gratings, spherical and cylindrical lenses, waveguides and artificial holograms) by subsequent selective etching in aqueous and/or non-aqueous etching solvents. The profiles of the structures produced by etching, were subsequently measured using the AFM and the reflection electron microscopy (REM) techniques.

## 3. Results

Our experiments give evidence that chalcogenide glassy materials of all studied systems are photosensitive and structural changes in short range order (SRO) can proceed into the structure of as-evaporated (virgin) thin films by exposure to broad band sources (e.g. halogen lamp) as well as by monochromatic light of  $\text{Ar}^+$  laser and/or He–Cd laser. These photostructural changes in SRO are most significant for thin layers of As–S, particularly for those with As over stoichiometry (Fig. 1). It has been found that layers deposited by spin coating method have in general lower photosensitivity than layers of the same composition produced by evaporation.

The selectivity of the dissolution (defined as the etching rate ratio of exposed and unexposed material) as a function of thin layer composition, its prehistory as well as of etching bath composition was investigated. It was found that arsenic based films have higher selectivity of etching than Ge based films in used etching solvents (aqueous sol-

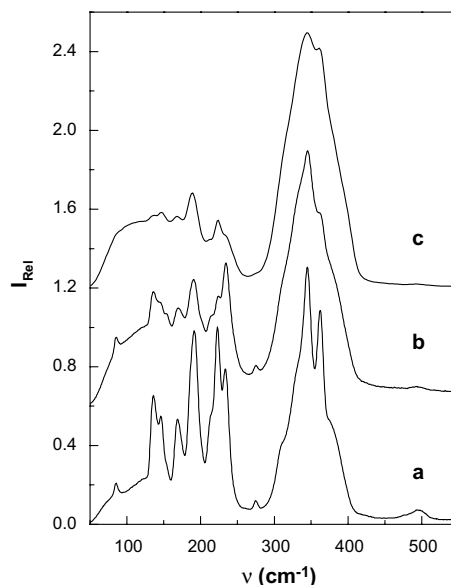


Fig. 1. Raman spectra of  $\text{As}_{42}\text{S}_{58}$  thin layers as-evaporated (a) and exposed (b) and of bulk sample (c). Exposure time 30 min, halogen lamp with 20  $\text{mW}/\text{cm}^2$ .

vent NaOH + Na<sub>2</sub>CO<sub>3</sub> as well as amine based non-aqueous solvent). Both positive and negative selective etching can be achieved depending on the composition of the film and etching solvent used. In general higher selectivity of etching is achieved for As rich samples in aqueous solvents and exposed part dissolves more quickly (positive etching). Contrary higher selectivity can be found for S (Se) rich films in non-aqueous solvents and dissolution of exposed part takes longer time (negative etching). Thus for example for the stoichiometric As<sub>40</sub>S<sub>60</sub> films we achieved both positive and negative etching using different etching baths.

On the base of these fundamental studies of photostructural changes of optical properties and chemical resistance to alkaline solvents we formed in the next step diffraction gratings in thin chalcogenide layers. All three applied exposure techniques (exposure through Cr mask, holographical exposure and direct laser writing) were successively applied to create diffraction gratings. The diffraction efficiencies  $\eta_{1T}$  (defined as the power ratio of the light diffracted into the first transmitted order to the incident light) of these amplitude type gratings at  $\lambda = 632.8$  nm have been up to 3% for normal incidence. This relatively low diffraction efficiency even decreased slowly with time when films were kept at normal laboratory conditions. Therefore, we transformed these relatively unstable gratings into stable corrugated surface reliefs using selective etching. Examples of such sinusoidal grating with a period 2  $\mu\text{m}$  and crossed grating with a period 370 nm are shown in Fig. 2.

The diffraction efficiency of amplitude/phase gratings after their transformation into relief type increased remarkably. For example the diffraction efficiency (DE) of gratings with a period of 2  $\mu\text{m}$  written by holographical exposure and consequent etching in amine based solvent reached up to 29% in both first (1T) and minus first (-1T) transmitted diffraction orders for normal incidence and at wavelength of 632.8 nm. The optimal exposure dose was in the range 6–24 J/cm<sup>2</sup> for layer thickness between 245 and 1350 nm. The mean DE of gratings prepared by direct laser writing method was up to 25% for the same grating period and the diffraction conditions given above.

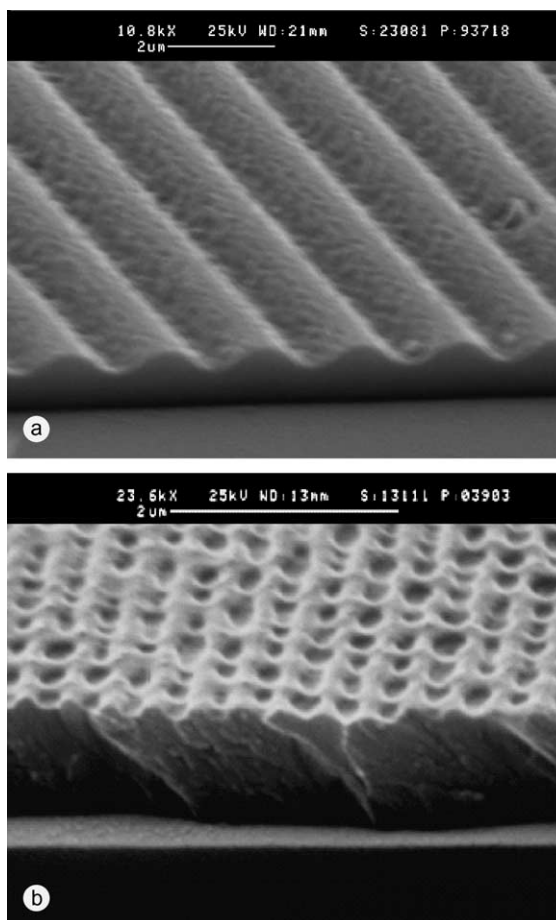


Fig. 2. REM picture of sinusoidal grating with a period 2  $\mu\text{m}$  (a) and crossed grating with a period 370 nm (b) formed in As based chalcogenide thin layers.

#### 4. Discussion

It is well known that the structure of as-evaporated chalcogenide films can be significantly different from those of exposed films [3]. Large concentration of 'wrong' homopolar bonds is in many cases the reason of thermodynamical instability of such structures. Exposure with suitable light can induce chemical redistribution and the structure of the thin layer becomes comparable to the structure of bulk sample. In agreement with this explanation the intensity of the Raman signal at the band 364 cm<sup>-1</sup>, and also of the group of narrow bands in the range 120–220 cm<sup>-1</sup>, which

correspond to the presence of As–As bonds [4], decreases significantly (see Fig. 1). Furthermore the signal at the band at  $495\text{ cm}^{-1}$ , corresponding to the presence of S–S bonds [4], is diminishing fully during exposure. For spin coating the structure of as-prepared layers is already very similar to the structure of bulk samples and thus layers prepared by this technique have lower photosensitivity.

The photoinduced structural changes resulted in changes of the optical transmissivity and refractive index in exposed parts of films. Thus, in general, exposed parts of As based films became photodarkened ( $\Delta\lambda = 0\text{--}80\text{ nm}$  for  $T = 10\%$ ) and their refractive index increased ( $\Delta n = 0\text{--}0.12$ ). Contrary Ge based thin layers were photobleached ( $\Delta\lambda = 0\text{--}40\text{ nm}$  for  $T = 10\%$ ) and their refractive index decreased ( $\Delta n = 0\text{--}0.1$ ). The values of  $\Delta T$  and  $\Delta n$  depend on composition of films and conditions of exposure; details will be published elsewhere soon. Thus with all applied exposure techniques amplitude/phase type DOEs were prepared. Diffraction efficiency of these gratings was up to 3% only. Gradual decrease of their diffraction efficiency with time can be explained by gradual photostructural changes induced by day light in those parts of the films, which were not illuminated during grating exposure.

Surface relief-type gratings (period  $2\text{ }\mu\text{m}$ , etching depth approximately  $250\text{ nm}$ ) prepared by optical exposure and subsequent selective etching (either positive or negative) showed high diffraction efficiency (about 25% in  $1T$  and  $-1T$  at normal incidence and  $\lambda = 633\text{ nm}$  for all recording techniques). This value is close to the theoretical maximum of 29% for a grating with ideal sinusoidal surface profile and of 33% for binary gratings etched into the applied chalcogenide glass with a refractive index of 2.45. Owing to the flexibility and to the demonstrated applicability of short wavelength direct writing laser lithography for the structuring of thin chalcogenide layers a variety of different diffractive optical elements with small feature sizes can be fabricated. Fig. 3 shows, for example, part of an array of diffractive lenses written by this technique.

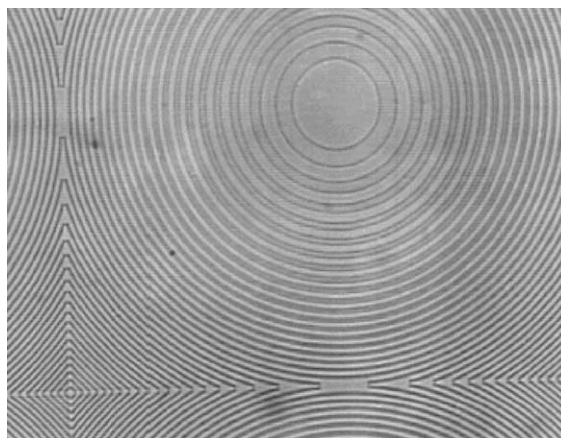


Fig. 3. Microphotography of planar lens array written in As based chalcogenide by direct writing laser lithography and consequently etched using amine based solvent.

## 5. Conclusions

Possibilities of holographic recording and direct writing laser lithography usage for production of DOEs with feature sizes between  $0.37$  and  $4\text{ }\mu\text{m}$  in thin layers of amorphous chalcogenides have been shown. Selective etching of chalcogenides in alkaline solvents was used to increase significantly the diffraction efficiency of recorded DOEs.

## Acknowledgements

This work was financially sponsored by MSMT Czech Republic and International Bureau of German BMBF at DLR through project CZE-00-012.

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