

# Light and electron beam induced surface patterning in Ge-Se system

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Homogeneous Ge<sub>x</sub>-Se<sub>1-x</sub> thin layers have been prepared by thermal evaporation and pulsed laser deposition technique. Geometrical structures were formed on the surface of the chalcogenide samples by electron beam and photon irradiation methods. The morphology of the created reliefs was investigated by atomic force microscopy. The different aspects of the mechanism of surface relief recording were studied, together with the dependence of the surface relief profile heights on the chalcogen concentration. In addition, the compositions and recording parameters giving the best results were determined.

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## 1. Introduction

Amorphous chalcogenide glasses are well known as optical memory materials in which different stimulated processes like photo-darkening and bleaching, local expansion or contraction, mass transport, change of transmission, absorption, and refractive index take place (1-6). It is known that irradiation of amorphous chalcogenide thin films with bandgap light or electron beam can result in significant optical, structural and volume transformations. These could be used to prepare various surface structures on the films.

The direct, one step process of surface relief formation was found to be connected with induced mass transport in the chalcogenide material under non-uniform irradiation (7-9). Since the structure of these materials is rather sensitive to any energy input, electron beam irradiation can be used to produce surface structures as well (10, 11). These phenomena are studied in detail mainly for the As-Se(S) system (7-13). There is only some information available concerning the surface patterning in Ge-Se samples (14-17), and the mechanism of these processes is generally not completely clear

Chalcogenide thin films can be obtained by different techniques such as radio-frequency sputtering, thermal vacuum evaporation (TE) or even pulsed laser deposition (PLD) (18-21). The TE and PLD were successfully used to create single and multilayer amorphous chalcogenide nano-structures (19-23). In this work we used both TE and

PLD methods for the preparation of Ge-Se thin layers. Our aim was to investigate the structures formed by light and electron beam irradiation, as well as the compositional dependence of local volume changes in the created films. Finally, our attention was directed to find out the best recording conditions for the studied materials, which could eventually be used for the creation of surface relief elements for different applications.

## 2. Experimental

Bulk chalcogenide glasses from Ge-Se system were synthesized in silica ampoules from high-purity (typically 99.999%) elements by melt-quenching method and used for the deposition of amorphous layers via the both above mentioned techniques. For the TE method a Cressington 308R thermal evaporation system was used at  $1 \times 10^{-6}$  mbar pressure, using a semi-Knudsen cell crucible from sources with compositions of Ge<sub>24</sub>Se<sub>76</sub> and Ge<sub>30</sub>Se<sub>70</sub>, resulting in formation of films with compositions Ge<sub>28</sub>Se<sub>72</sub> and Ge<sub>33</sub>Se<sub>67</sub>. With PLD preparation technique thin films with compositions of Ge<sub>24</sub>Se<sub>76</sub> and Ge<sub>30</sub>Se<sub>70</sub> were prepared from Ge<sub>20</sub>Se<sub>80</sub> and Ge<sub>27</sub>Se<sub>73</sub> bulk glasses. PLD setup consisted of a KrF excimer laser (248 nm,  $300 \pm 3$  mJ per pulse, 30 ns pulse duration, 20 Hz repetition rate) and a vacuum chamber (background pressure  $< 4 \times 10^{-4}$  Pa). The substrates used for PLD (chemically cleaned microscope glass slides and Si wafers) were positioned parallel to the target

surface at a target to substrate distance of 5 cm. The laser energy fluency on the target was set to  $\sim 2.6 \text{ J.cm}^{-2}$ .

The composition of the samples was determined by Energy Dispersive X-Ray Spectroscopy (EDS) using Hitachi S-4300 Scanning Electron Microscope (SEM) system. It was established, that the composition of the final material differs from the precursor material, and the difference depends on the Ge content of the precursor material and on the preparation method. Ambios XP-1 profilometer was used to determine the sample thickness before and after laser irradiation and heat treatment. The thickness  $d$  of the samples was controlled by the calibrated evaporation and deposition processes and was about 1000 nm for the TE and 500 nm for the PLD samples.

Holographic recording was made by polarized laser beams (DPSS laser,  $\lambda = 532 \text{ nm}$ , output power  $P = 27 \text{ mW}$ ). As a result of the treatment a grating with  $6 \mu\text{m}$  period was created. The surface gratings were created through 4 hour recording cycles. In this way the simplest surface structures – holograms, diffraction gratings – were recorded with a setup on a Newport table by two interfering laser beams, usually at p-p polarization conditions with additional s-polarized illumination for the enhancement of the recording process (24). Besides of the light, electron beam was also used to create structures. Acceleration voltage of 30 kV, and 10 nA specimen current were used to irradiate the samples. Multiple line scans by e-beam focused into a spot of 50-70 nm diameter were performed on each sample with different periods of time, i.e. with increasing total exposure. The created surface structures were investigated by a Veeco diCaliber atomic force microscope (AFM) which also gave information about the average height of the created structures. The samples were investigated in tapping mode with TESP-MT tapes. For the determination of averages the gratings were investigated in 10 different places. The error of the measurements was about 2-3%.

### 3. Results and discussion

Holographic gratings were created as a result of the interference of two coherent beams in p-p polarization mode at the surface of the Ge-Se films. It was shown earlier that additional s-polarized beam could enhance the recording process so it was used in our case as well, while the beams have equal intensity (24). The maximum efficiency of laser-matter interaction for chalcogenide materials occurs at photon energies being equal to the optical absorption edge of the given compound. Because of that, we have selected green laser illumination for Ge-Se samples (25, 26). Formation of good quality surface patterns was achieved.

Typical AFM image of the recorded holographic gratings are shown in Fig. 1. The grating is highly uniform. Its period is approx. 7 microns and the height (distance between the lowest and highest points) is around 0.5 microns.

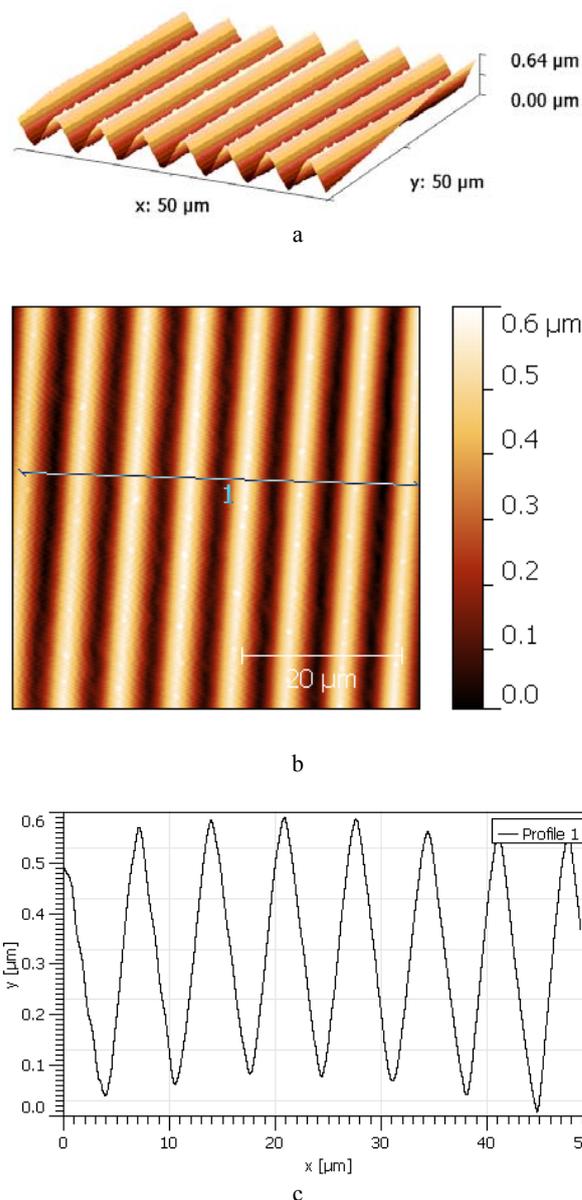


Fig. 1. AFM image of the holographic grating with 2D (a) and 3D representation (c) and a cross section obtained at the indicated marker (b) on  $\text{Ge}_{24}\text{Se}_{76}$  chalcogenide thin film.

The compositional dependence of the surface deformation (characterized by half-height  $h/2$  of the sinusoidal profile of the diffraction grating) gives information on the efficiency of the recording of surface holographic grating. According to Fig. 2 the composition giving the best (or highest) grating is  $\text{Ge}_{24}\text{Se}_{76}$  - the simplest one, being stable and containing the smallest amount of Ge among the other similarly stable  $\text{Ge}_x\text{Se}_{100-x}$  compositions (see Fig. 2).

The increase of the irradiation time results in higher profile heights in gratings that can reach even the total thickness of the layer. This means complete mass transport from the illuminated to the dark regions. Comparison of these findings on Ge-based chalcogenides with our previous work on As-based ones (27) shows that the lower sensitivity of germanates probably arises from the lower photo-plasticity of these materials, giving higher rigidity of the glass network.

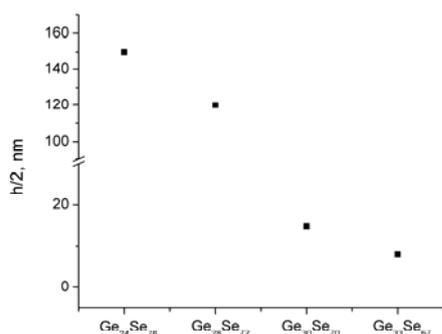


Fig. 2. Dependence of half heights of the recorded grating profiles on composition. The gratings were prepared with equal exposures ( $1 \text{ kJ/cm}^2$ ).

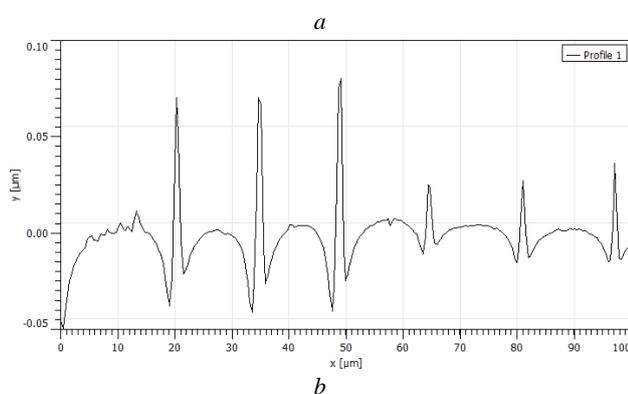
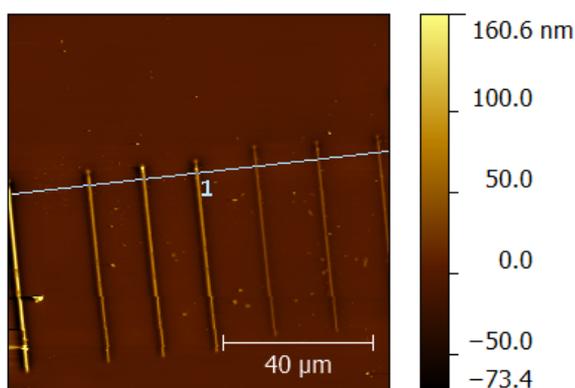


Fig. 3. 2D AFM image of the electron beam induced surface patterns (a) and the corresponding cross section obtained at the indicated thin marker (b) on  $\text{Ge}_{24}\text{Se}_{76}$  chalcogenide thin film.

Ge-Se samples on an ITO covered glass substrate were mainly used to investigate surface relief recording by focused electron beam (see Fig. 3). It can be seen that the irradiation resulted in remarkable changes in the surface relief in the surroundings of the treated regions. Narrow walls were formed along the irradiated line with valleys on both sides. These valleys correspond to the region from where the mass transport occurred. The different lines on the surface were irradiated by electron beam focused into a spot of 50-70 nm diameter with different irradiation times. The cross section clearly indicates the dependence of the height of the surface relief on the treatment time of each line. Fig. 4 compares the average half height values obtained for the samples of different composition. A similar compositional dependence can be observed for electron beam recording as it was established for light induced surface patterning. The highest surface relief with this recording method was again obtained for the  $\text{Ge}_{24}\text{Se}_{76}$  composition.

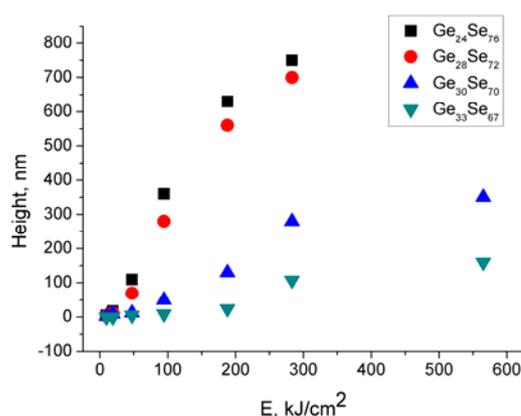


Fig. 4. Profile heights of e-beam recorded lines on the surface of different Ge-Se compositions vs. exposure by electron beam.

Based on the above shown results it can be concluded, that the efficiency of light and electron beam stimulated volume change increases with increase content of Se in Ge-Se films. The most significant volume changes during recordings were observed for  $\text{Ge}_{24}\text{Se}_{76}$  and  $\text{Ge}_{28}\text{Se}_{72}$  samples. The large width of the created lines could be connected with the scattering profile of the electrons in these materials, as it was modeled in our previous work (10,11), and could be reduced by decreasing the time of irradiation and the penetration depth of the electrons.

The efficiency of the surface structure recording in chalcogenide glasses essentially depends on the composition, independently of the way of the energy input. The excitation of electron-hole pairs, defect creation, bond breaking and rearrangement are always present in these amorphous semiconductor materials under treatment with either photons or electrons. As a consequence, the sample possesses increased free volume (2) and plasticity (28), which play important role in the relatively small (about

0.5-1%) local expansion effect in irradiated spots, and also influences essentially larger local surface (thickness) changes due to the stimulated mass-transport in the gradient fields of excitation (9,12,28). We suggest that the lone Se atoms formed dynamically during the treatment play an important role in these stimulated processes. On the microscopic level light and electron beam induced volume changes could be connected with electron-hole pair excitation, defect creation, bond breaking and rearrangement. These processes are mainly related to and induced by the Se atoms, the bonds of which are sensitive to appropriate illumination. This appears as lateral mass transport on the macroscopic level, controlled by volume diffusion. The importance of Se atoms in light and electron beam induced surface patterning is clearly indicated by the compositional dependence of the efficiency of the process, manifesting in a remarkably decreasing reaction of the material to light illumination with increasing Ge content (26). So the structural changes should be investigated to make clearer the role of Se atoms in the process, which occurs during irradiation by photons and electrons.

Our results obtained on light and electron induced volume changes demonstrate the potential of materials from the Ge-Se system for surface relief recording, as it was investigated and presented for As-Se and As-S layer structures (7,11, 12, 28).

#### 4. Summary

Light and electron beam induced surface patterning was studied in thermally evaporated and pulsed laser deposited Ge-Se samples.

The height of the produced geometrical structures was determined and investigated. A compositional dependence was established in these samples, according to which the efficiency of light and electron beam induced volume changes increase with the Se content in Ge-Se thin films. The surface patterning results from small local volume expansion-contraction at the initial stage of structural transformations but depends mostly on mass transport at the surface of the material at the longer time scales, high exposures. It can be concluded that Se atoms have an important role in the light and electron beam induced changes in chalcogenide materials, which requires more detailed investigations.

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