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Nanostructuring of chalcogenide glasses using electron beam lithography

M. VLCEK[a,b*], H. JAIN[a]
[a] *International Materials Institute for New Functionality in Glass, Lehigh University, Bethlehem, PA, 18015, USA*
[b] *Department of General and Inorganic Chemistry, FCHT, University of Pardubice, Pardubice 530 12, Czech Republic*

We have investigated nanostructuring capabilities of As-S chalcogenide glasses using electron beam lithography. After exposure to electron beam the thin films of these inorganic glasses can be etched in alkaline amine solvent with high selectivity. Dissolution rate is linearly proportional to the electron dose and Gaussian electron beam intensity profile is well replicated in the shape of individual lines. High resolution smooth, shaped nanostructures have been fabricated in chalcogenide thin films with dimensions well below 100 nm and aspect ratio about 3.

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1. Introduction

Amorphous chalcogenide glasses are well known group of inorganic materials with a number of remarkable and unique properties. One of the most studied phenomena in these glasses is based on photoinduced change in chemical properties on exposure to bandgap light (typically in the visible or near infrared (NIR) region of the spectrum) [1,2]. It has demonstrated potential application of chalcogenide glasses in the fabrication of diffractive optic elements (DOE) with high refractive index and IR transmitting properties [3, 4], fabrication of photonic-band-gap structures [5-8] and as high resolution inorganic resists for lithography [9, 10]. Being glass, they exhibit higher resolution capability than the currently used polymers, as expected from the small size of the fundamental structural units and strong covalent bonds in the former. The very high resolution is realized by exploiting the fact that the structure of these inorganic glasses is also sensitive to UV [11, 12] and electron beam (e-beam) [8, 13] as well as X-rays [14]. Any of these forms of radiation produces sufficiently different chemical resistance of the exposed and non-exposed parts to a variety of etchants to be useful in their high resolution structuring. Both, positive and negative etching can be achieved depending on the composition of the sample, its preparation history, the conditions of exposure and etching, etc. [2, 11].

Our objective in this paper is to assess the nanostructuring capabilities of As-S chalcogenide glasses by wet etching. We have specifically examined the effect of electron beam, which can be readily focused to the diameter of ~1 nm and therefore forms the basis of nano-lithography. Our previous studies on microstructuring in chalcogenide glasses established organic alkaline solvents to be generally superior etchants (fewer problems with adhesivity, swelling etc.) [11]. Therefore, after e-beam irradiation we applied amine based solvents as the etchant for separating the exposed and unexposed regions.

2. Experimental details

Bulk samples of As_xS_{100-x} (x = 33 - 42) glasses were prepared by melting high purity (5 N) elements in evacuated quartz ampoules for 8 h at 650 ^oC in a rocking furnace. After synthesis, the ampoules were quenched in cold water. Thin films with thickness 100 - 400 nm were deposited onto microscope slides pre-deposited with a thin Cr layer (10 nm) by the thermal evaporation method (starting pressure 6.10^{-6} Pa) using resistance-heated silica crucible. The deposition rate of the As-S films was about 1 nm/s. To minimize the uncontrolled photoinduced effects produced by ambient light, very low-level red illumination was used in the laboratory during preparation and subsequent handling.

Electron beam lithography (EBL) experiments were conducted using LEO 1550 VP lithograph with accelerating voltage 30 keV, beam current ~ 40 pA, and line exposure dose between 1 and 10 nC/cm. The results were compared with those obtained by traditional photo lithography using halogen lamp exposure (30 mW/cm^2) through chromium mask. Written nanostructures were subsequently developed using amine based alkaline solvents. After completion of the process, the fabricated structures were observed by scanning electron microscopy using the same instrument as for writing. The thickness remaining after etching as well as the topography of lines/wheels was determined using an atomic force microscope (AFM, model D 3000, Digital Instrument).

3. Results and discussion

To determine the resolution of nanostructures created in chalcogenide glass we fabricated seemingly simple but

informative test patterns such as a wheel. The study of such patterns allows assessment of the e-beam sensitive material to form separate straight and curved lines. One can also obtain resolution from the observation of fine structures formed in places of crossing and overlapping of separate lines that form the wheel.

Wheels with 10 μm diameter and lines 200 nm in width were written by e-beam into arsenic chalcogenide thin films. Contrary to organic resists, we could not see written structures in our films immediately after writing with the electron beam. The structures became visible only after developing in amine based alkaline solution, when a negative type of etching was observed, i.e. exposed parts (wheel or the lines) were less soluble than the unexposed part. The time of etching in alkaline bath was usually between 30 sec to 120 sec and depended on the composition of the chalcogenide film, exposure dose, composition and concentration of etching bath. Negative etching proceeded as well when samples were exposed to broad wavelength optical source (halogen lamp) through Cr mask to produce 10 – 100 μm size features. The difference between the electron and light exposed samples was that the features were visibly photodarkened only for the latter exposure of stoichiometric and As rich films.

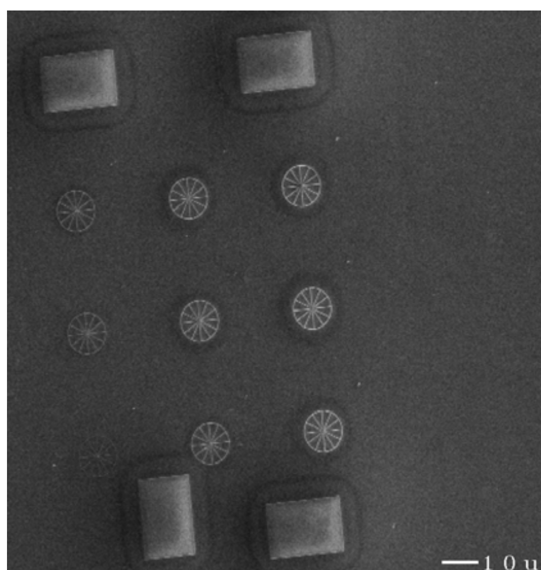
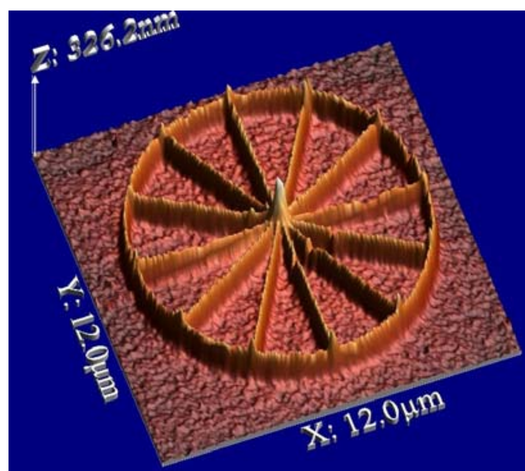
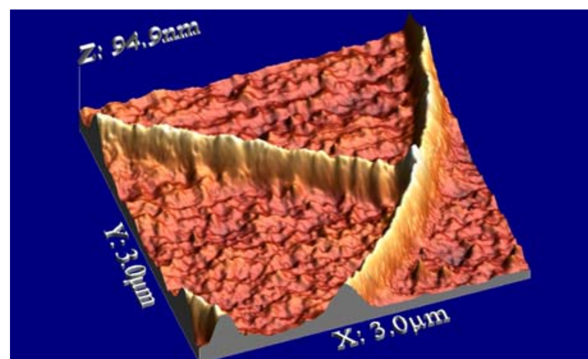


Fig. 1. Optical microscope picture of "nanowheels" fabricated by electron beam lithography. The wheels were written in As-S thin film with different electron dose and then etched in alkaline amine based solution.

The optical micrograph of a set of 9 wheels is presented in Fig. 1, which were fabricated by irradiating with different electron dose followed by wet etching. The 3-D AFM image of one of these wheels is shown in Fig. 2 together with image of a section of such wheel. In the place of intersection of two lines within the wheel, the height of the film remaining after etching is clearly higher than the value for the single line. In the central part of the wheel, where a total of six lines intersected, the height of the apex of the cone shape structure in Fig. 2a is still much higher. Thus we note that for the same time of etching the relative height of exposed and unexposed regions depends sensitively on the total electron dose. The etching rate of unexposed film was about 4 nm/sec, but it dropped practically to zero (< 0.1 nm/sec) when high doses were used. A quantitative analysis of various wheels shows that the thickness of the film remaining after constant time of etching is linearly proportional to the dose of e-beam exposure (see Fig. 3). So, for example, in the places of intersection of two lines where the film was exposed twice, the height of the film was also about two times higher than away from the intersection. At the centre of the wheel, where altogether 6 lines intersected, the thickness of the film after the etching was about the same as the starting thickness of the film (330 nm). Therefore, we may conclude that when sufficiently high electron dose is used, the chalcogenide film becomes essentially insoluble in amine based solvents at least for the time of etching used here (a few minutes).



a



b

Fig. 2. The 3-D AFM pictures of one of the "nanowheels" (a) shown in Fig. 1 (initial thickness d_o = 330 nm) and of the fragment of the "nanowheel" demonstrating Gaussian shape of individual lines (b).

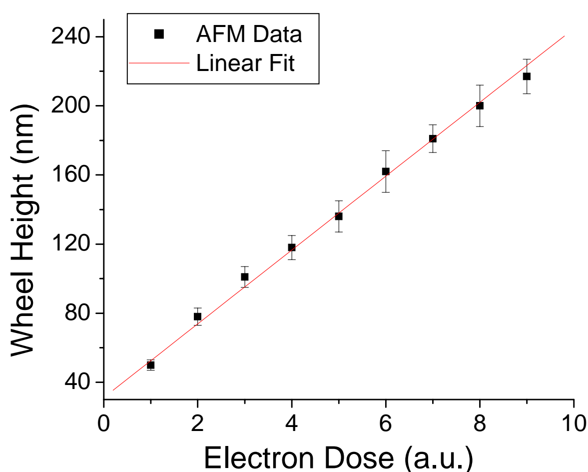


Fig. 3. Thickness of the As-S thin film remaining after etching as a function of electron dose. Experimental points are taken from measurements of heights of wheels in Fig. 1.

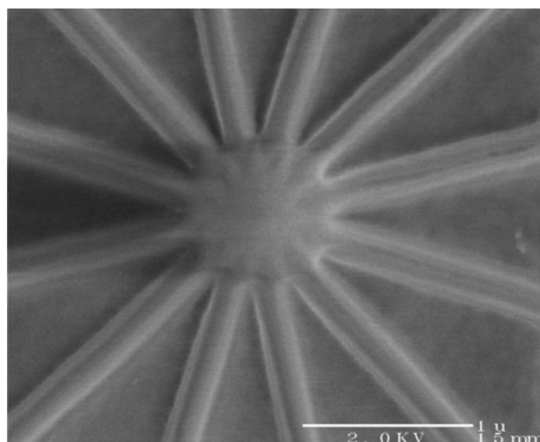


Fig. 4. SEM picture of the central part of a "nanowheel" fabricated into As-S thin film.

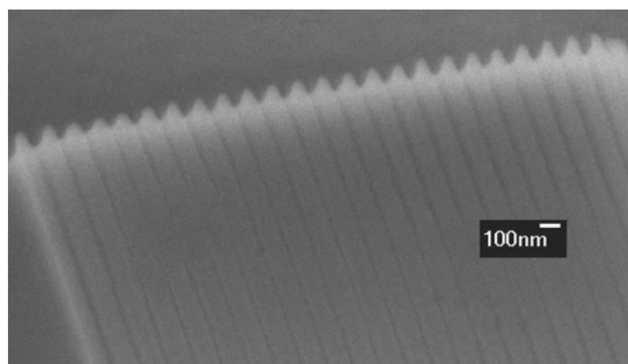


Fig. 5. SEM picture of a nanograting fabricated in As-S film by electron beam exposure followed by development in amine based solvent. Stage tilt of 45° at 15 kV.

The wheel or any other structure is formed by lines written by electron beam which has Gaussian intensity profile. This is why the cross-section of individual lines has the same shape (see Fig. 2 b) however the width of lines is significantly larger than the diameter of writing e-beam itself (~ 1 nm). The final width of the written lines is apparently determined by the scattering of secondary electrons, which are produced by the primary beam itself. One must keep in mind that electrons are not the only particles emitted when the e-beam strikes the sample. X-rays, photons and electrical charge are also present and can influence final shape of the etched lines. We find that the combined effect of all these particles maintains the Gaussian distribution with the center located at the well-focused primary e beam. A consequence of Gaussian profile and high sensitivity of etching to electron dose is also nicely seen at the center of the wheel in Fig. 2 a, where a smooth three dimensional cone is formed with Gaussian symmetry.

For the assessment of resolution capabilities of the arsenic sulfide glass films, it is useful to examine the intersection regions of the wheels, where lines approach each other. From the examination of one such region shown in Fig. 4, it seems that a resolution of better than 20 nm can be expected for these materials. And indeed we fabricated regular periodic structures which consist of an array of 30 nm wide individual lines; the adjacent lines are separated by about 15 nm wide grooves (Fig. 5). The aspect ratio of prepared structures is estimated to be about 3.

We have determined that the chemical resistance of amorphous arsenic chalcogenide films to alkaline amine solvents is similarly increased whether exposed to the e-beam or the visible light. In both cases, exposure significantly decreases the dissolution rate, indicating a negative lithography response of chalcogenide film. Thus we may assume that similar mechanisms may operate for the photo as well as e-beam lithography. In both cases, the interaction of the chalcogenide film with applied photon and/or electron flux results in the changes of the internal glass structure but the amorphous state of the film is preserved. This ability to change chemical structure by electron beam exposure, while preserving amorphous character of the structure, enables very fine nanostructures to be fabricated in these materials by electron beam lithography. The theoretical resolution limit of chalcogenide based resist itself should be the diameter of molecular building units (≈ 1-2 nm). Of course, in practice, the scattering of secondary electrons will decrease the resolution limit, which is yet to be established.

From the data in Fig. 3 we note that even for the shortest electron beam exposure, the structure of the film was influenced by electron beam uniformly in the whole

thickness of the exposed chalcogenide film. This observation is in good agreement with the results of Nishihara [15] who found that 25 kV electron beam penetrates and modifies the film properties at least one order deeper than the thickness of our films. Significant decrease in dissolution rate, which can be smoothly modulated with electron beam exposure, opens up the possibility of forming shaped nanostructures in chalcogenide glasses. Further studies of this nanofabrication feature are in progress.

4. Conclusion

We have clearly established the nanostructuring capabilities of chalcogenide glass films by electron beam lithography. We confirmed that, similar to exposure by suitable photons, exposure of arsenic sulfide films by electron beam significantly enhances their chemical resistance to alkaline amine based solutions. The increase in chemical resistance is linearly proportional to the electron dose. Thus smooth, shaped nanostructures (width of motives tens nanometers) can be easily fabricated in these films. We believe that even finer resolution should be possible in an inorganic glass by optimizing the film thickness, electron beam energy, etching conditions, etc.

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*Corresponding author: miroslav.vlcek@upce.cz