

Nonlinear photoresist films fabricated by coevaporation of As₂S₃ glass and silver

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Silver metal evaporated below or above a layer of As₂S₃ glass are known to propagate under action of light within the glass layer and strongly modify its photochemical properties. We demonstrate that when silver is co-evaporated together with the glass, and within a certain range of silver concentration, this property is conserved locally. This leads to a new kind of photosensitive effect in the chalcogenide glass with completely new photoresist properties such as giant contrast and superlinear dissolution. These new properties make silver doped As₂S₃ glass an ideal material for the fabrication of three-dimensional structures with sub-micron feature size. The effect is explained within a percolation model. The advantages of superlinear photoresists, especially for the case of maskless photolithography, are shortly discussed

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1. Introduction

The interest to inorganic chalcogenide glassy photoresists has increased considerably in the recent years because of growing application of these materials for solution of different tasks of modern microelectronics and optoelectronics [1-7]. Chalcogenide photoresists have several advantages like very high resolution, high etch selectivity, good stability, possibility to be used both on planar and non-planar substrates, together with high refractive index 2.5 – 3.5 and transparency in the IR range. With amine-based developers chalcogenide photoresists can work in positive, negative and lift-off photolithographic processes. These properties are important for different applications, particularly application in micro-optics [3] and fabrication of photonic crystals [7]. Direct laser writing of three-dimensional photonic crystals with a complete photonic bandgap was performed, using As₂S₃ chalcogenide photoresist [1]. In many cases chalcogenide photoresists having two-layer structures: chalcogenide film - Ag-layer were used [9, 10]. These negative type photoresists, used with alkaline developers, are based on the photoinduced diffusion of silver into chalcogenide film. All the above-mentioned photoresists have linear development characteristics, where the increased radiation dose led to gradual increase of dissolution time.

Recently we developed new chalcogenide photoresists in which contact Ag-chalcogenide film was realized in the entire volume of photoresist [11]. They were fabricated using vacuum co-evaporation of As₂S₃ glass and Ag. These photoresists were shown to have superlinear dissolution characteristics. Increasing of the dose of irradiation led to very strong super-linear increase of dissolution time. Such photoresists, having giant contrast, are prospective for many photolithographic processes like holographic lithography, zone-plate lithography and other cases of maskless photolithography, especially for

interference lithography of photonic crystals, directly written in the high index resist materials.

In the present paper we consider more thoroughly the properties of photoresists fabricated by co-evaporation of Ag with As₂S₃ glass. Particularly, the influence of irradiation source and the composition of the developer on the photoresist characteristics are studied. Change in dissolution time after annealing of the photoresists and also comparative investigation of the influence of Ag-doping and annealing on dissolution and photodarkening characteristics of the As₂S₃ films provide additional arguments for explanation of the superlinear behavior of the photoresists. We used Auger spectroscopy for determination of the Ag distribution in the film and Raman spectroscopy for understanding of possible changes in the films structure. Some advantages of the non-linear chalcogenide photoresists application will be also discussed.

2. Experimental

Thin Ag-doped films of As₂S₃ were prepared by thermal coevaporation of crushed glassy chalcogenide material from a quartz crucible and Ag wire from a tungsten boat in vacuum of (1-3) x 10⁻⁶ Torr. Keeping the constant evaporation rate of Ag, we varied the rate of chalcogenide glass evaporation and fabricated the samples with different Ag concentration in the range of 0.5 – 9.0 wt %. The thickness of all films was in the range of 0.5-2.0 μm.

For assessing the Ag-distribution in the film we used Auger electron spectroscopy analysis combined with Ar-sputtering depth profile, allowing one to record the in-depth Ag distribution in the doped samples. For avoiding surface charging, the samples surface of the samples was covered by a thin Ni layer. The elemental composition of the samples was estimated by a SAM/AES/XPS apparatus

(PHI 549) with usual pressure of 1×10^{-9} Torr in the chamber and cylinder mirror analyzer.

A Hitachi U-1100 spectrophotometer was used in order to measure the transmission spectra in the non-irradiated and irradiated regions of the films. The refractive index spectra were calculated by the Swanepoel method [12], using the measured transmission spectra.

The changes in the film structure were followed by Raman spectroscopy, which was performed by a confocal Raman microscope (Jobin Yvon Labram UV HR). Raman scattering was excited by a diode laser at 784.79 nm with a power of ~ 10 mW. This wavelength is very essential, because irradiation of As_2S_3 films in this range causes no detectable photostructural transformations or photodoping effects. Spectra were monitored by focusing the laser beam with an $\times 50/0.75$ microscope objective to spots of ~ 1.5 μm diameter, on particular points of the sample. The scattered light was directed into a spectrometer via the coupled microscope (Olympus BX 41). The dispersive spectrometer was equipped with a 600 lines/mm grating and combined with a cooled charged coupled device (CCD) for Raman signal detection. A TV camera enabled to recognize the chalcogenide sample surface and to focus the laser beam on the point to be measured.

In the study of photoinduced dissolution, as the sources of irradiation we used a second harmonic of Nd:YAG laser (532 nm), radiation of a Hg-lamp and also solar radiation. In the cases of not very large time of dissolution, the rate of dissolution of irradiated and non-irradiated areas of the films was studied using a thin film interference technique. In this technique, the intensity of a semiconductor diode laser beam (910 nm), transmitted through the studied film during its dissolution, was recorded [13]. In the cases of very slow dissolution, the time of total dissolution was measured.

In all cases, the dissolution rates ratio, γ , was calculated, which is either the ratio of the rates of dissolution of non-irradiated and irradiated areas of the films, or the ratio of the time of total dissolution of irradiated area to the same for the non-irradiated area. In previous works, several amines were shown to have a very good selective effect (large γ values) for different chalcogenide films, therefore, in this study we also used various amine-containing selective developers. The most efficient negative selective developers were prepared on the base of morpholine, dimethylsulfoxide and ethanol.

3. Experimental results

3.1 Ag distribution, photodarkening, optical and Raman spectra

Fig. 1 shows the Auger depth profile of Ag and other components in one of the 3% Ag-doped As_2S_3 sample for various periods of the Ar ion sputtering. From this figure, it follows that the middle Ag concentration is really close to 3% but some non-homogeneous distribution of Ag exists, in spite of keeping constant the rate of Ag evaporation. The character of the Ag distribution is a little different in various samples, implying sometimes more and sometimes less homogeneous distribution in different Ag-doped films.

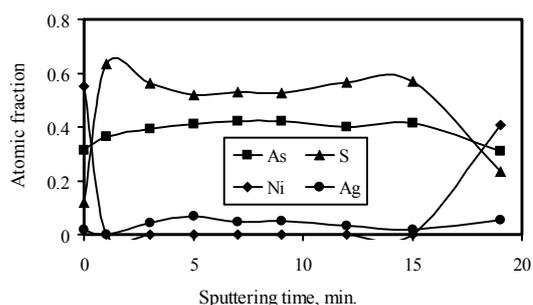


Fig. 1. Temporal variation of concentration of elements present in the 3% Ag-doped As_2S_3 film.

Transmission spectra for the 3% Ag doped and the non-doped As_2S_3 films having thickness ~ 2.0 μm are shown in Fig 2 and demonstrate a very weak influence of doping on the spectrum. The calculated values of refractive index are also very close for the doped and undoped films, for example, at $\lambda = 600$ nm they are 2.51 and 2.49, respectively, being very close to the literature data [14].

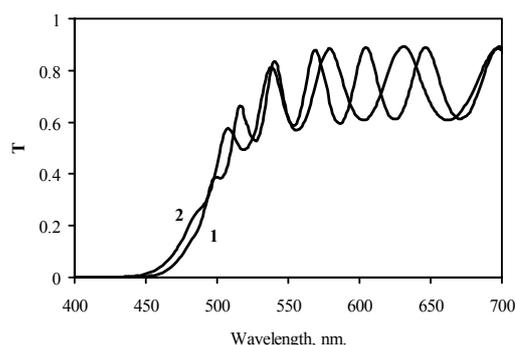


Fig. 2. Optical transmission spectra for the 3% Ag-doped (1) and non-doped (2) As_2S_3 films.

Results of comparative study of photodarkening effect under action of 532 nm light in the non-doped and doped films are shown in Fig.3. We can conclude that Ag-photodoping decreases the photodarkening values, but there are no drastic changes in the photodarkening process.

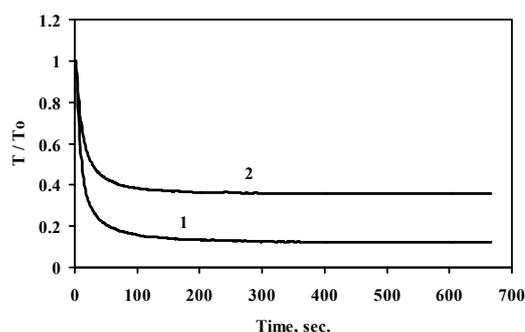


Fig. 3. Photoinduced change of optical transparency in the non-doped (1) and 3% Ag-doped (2) As_2S_3 films.

The typical Raman spectra of evaporated non-doped and 3 % and 9 % Ag-doped As_2S_3 films are compared in Fig. 4. The sharp bands in the spectra are signatures of one or more molecular species presented in the film. These spectra are very identical to the spectra observed by other researchers [10, 15-17]. The strong bands at 347 and 364 cm^{-1} are assigned to vibrations of the main pyramidal $AsS_{2/3}$ and As_4S_4 structural units of the chalcogenide glass. The numerous weak bands in the 70 - 240 cm^{-1} range, reported also in other papers [15, 16], reflect the existence of some non-stoichiometric structural fragments (As_mS_n -type) and S-S bonds.

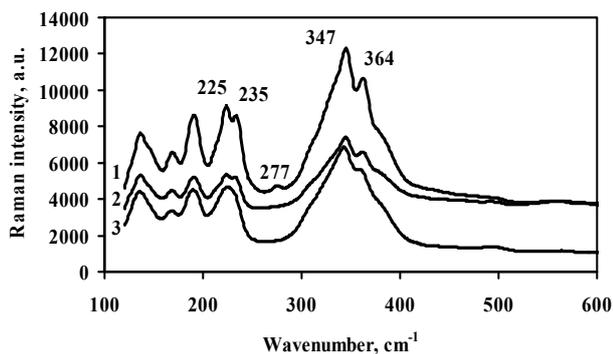


Fig.4. Raman spectra of non-doped (1) and also 3 % (2) and 9 % (3) Ag-doped As_2S_3 films.

It is important to mention that doping of the films even with 9 % of Ag affects the Raman spectrum only very weakly. The most distinct alterations are seen in the bands at 225, 235 and 277 cm^{-1} bands, and they can be some result of the Ag interaction with the sulfur atoms. Irradiation of the doped films also very weakly influence on the spectrum.

3.2 Photoinduced dissolution

Dependence of dissolution rates ratio γ on light intensity for the 5 minutes of irradiation for the non-doped and 3% Ag - doped films of 1 μm thickness is shown in Fig. 5. One can see that at low intensities both characteristics are nearly linear and very close to each other, but beginning from ~ 12 mW/cm^2 , the characteristic of the Ag-doped film starts to grow nonlinearly, achieving the very high γ values, while the curve of the non-doped film remains approximately linear. Fig.6 shows the γ versus the light intensity characteristics for the 3% Ag - doped film obtained with different irradiation times. All of them demonstrate the superlinear increase of the γ coefficient and besides, the light intensity, at which starts the non-linear growth of coefficient γ (threshold intensity), diminishes with the increase of irradiation time.

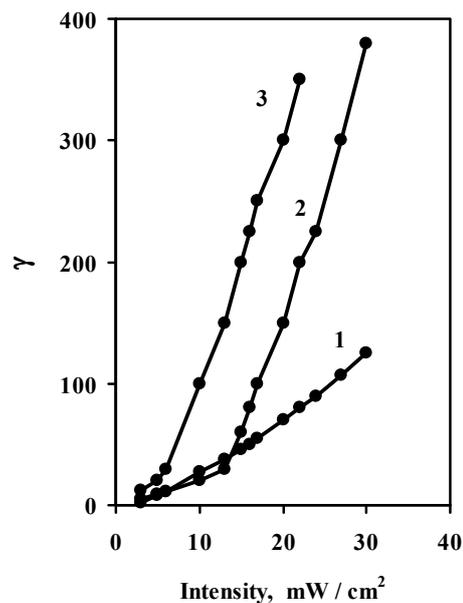


Fig. 5. Dependence of dissolution rates ratio γ on light intensity for the non-doped (1) and 3% Ag-doped (2) As_2S_3 films.

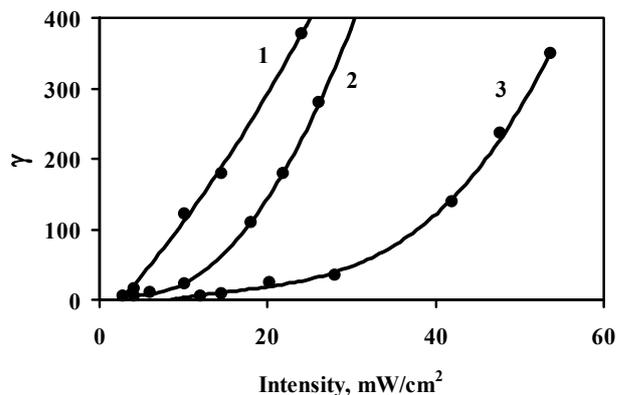


Fig. 6. Dependences of dissolution rates ratio γ on light intensity for the 3% Ag-doped As_2S_3 films.. obtained with irradiation times 10 min (1), 5 min (2) and 3 min.(3).

In Fig.7 we demonstrate characteristics $\gamma = f$ (irradiating time) in the non-doped and 3 % Ag-doped film of 1 μm thickness obtained at various values of laser light intensity. All characteristics for the doped film are also superlinear, and the critical irradiation time, indicating beginning of the nonlinear γ growth (threshold irradiation time), decreases with the increase of light intensity. Opposite, the characteristics in the non-doped film are linear and the γ coefficient has not so large values.

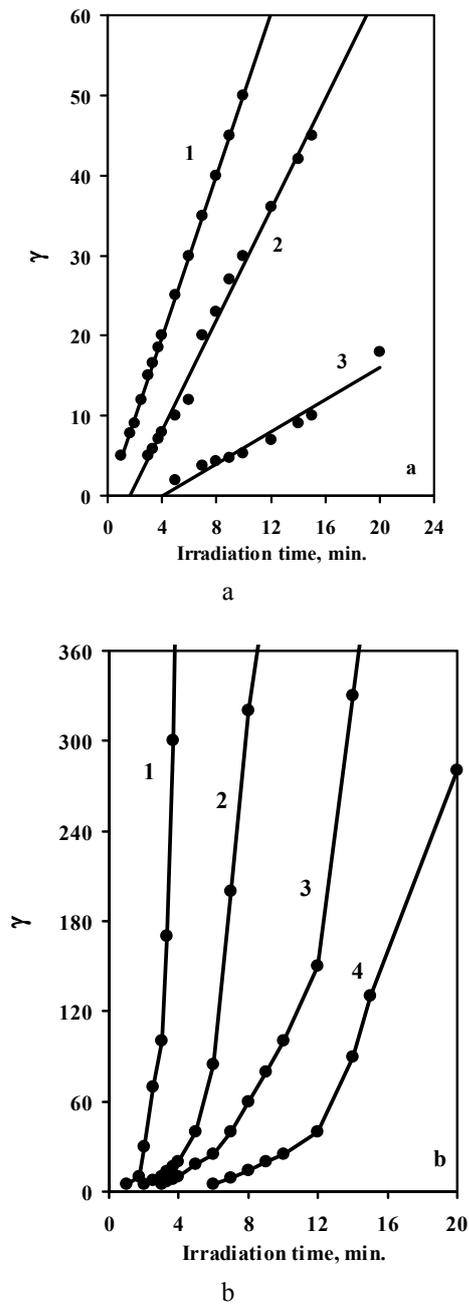


Fig. 7. Dependences of dissolution rates ratio γ on irradiating time for the non-doped (a) and 3.0 % Ag - doped (b) As_2S_3 films, obtained at various values of laser light intensity: 200 mW/cm^2 (a1 and b1), 130 mW/cm^2 (a2 and b2), 80 mW/cm^2 (b3) and 40 mW/cm^2 (a3 and b4).

Fig. 8 shows the dissolution rates ratio, γ , as a function of the dose of radiation (light intensity multiplied by irradiation time) received by the 1.5 % Ag doped photoresist of 1 μm thickness. These curves are obtained at three different irradiation times. Again we see two parts: steep and smooth growth of γ values. There is no complete coincidence of these curves and therefore we can not speak about an ideal fulfillment of the reciprocity law. But one can see that a certain number of absorbed light

quanta results in a transition from the smooth to the steep part of the dissolution process. The threshold number of quanta falling to the studied As_2S_3 (Ag) films was calculated as $\sim 1.35 \times 10^{19}$ quanta/ cm^2 .

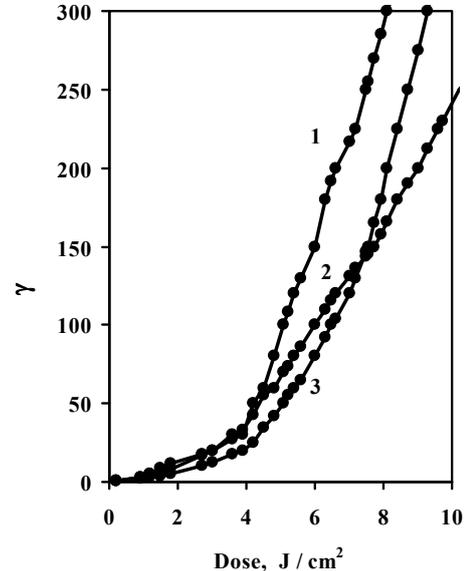


Fig. 8. Dissolution rates ratio γ as a function of the dose of radiation got by the 1.5 % Ag-doped As_2S_3 film at irradiation times of 10 min (1), 5 min (2) and 3 min (3).

Results similar to those shown in Figs. 5-8 were recorded for all studied As_2S_3 films doped with 1.0 – 3.5 % concentration of Ag, though specific form of different dissolution curves was strongly dependent on the level of doping, thickness of the film, light intensity and irradiation time.

3.3 Additional study of Ag-doped As_2S_3 photoresists

With diminishing Ag concentration, the nonlinear dissolution characteristic gradually transforms to the linear one, while at concentration larger than 3.5 %, even the non-irradiated As_2S_3 photoresist films practically cease to dissolve in this developer (sometimes we observed desisting of dissolution even in the non-irradiated As_2S_3 films doped with 3 % of Ag). Fig.9 shows a family of $\gamma = f$ (light intensity) characteristics obtained for the As_2S_3 films having approximately the same thickness 2 μm , doped with different amounts of Ag. All of them are characterized by the superlinear increase of the γ coefficient, but with increase of the doping level the strong increase of γ starts at lower light intensity and develops more abruptly. All the results described in the previous parts were obtained with Nd:YAG laser beam (532 nm) radiation. Irradiation of Ag-doped As_2S_3 films with other sources of radiation, particularly, with radiation of Hg lamp and solar radiation also leads to superlinear dissolution process.

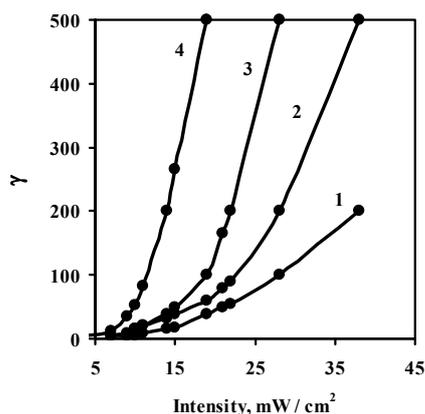


Fig. 9. Dependences of dissolution rates ratio γ on light intensity obtained for the As_2S_3 films having thickness $\sim 2 \mu m$, doped with 1.0 % (1), 1.5 % (2), 2.25 % (3) and 3.0 % (4) of Ag.

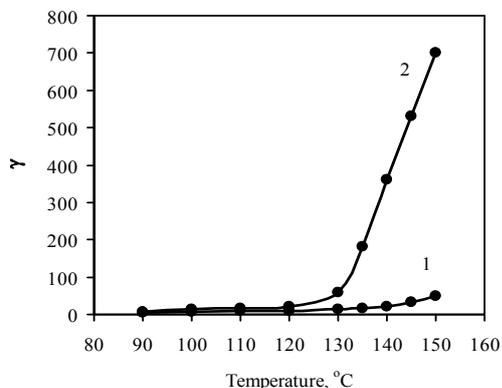


Fig. 10. Dependences of dissolution rates ratio γ of annealed and non-annealed films on the annealing temperature for the non-doped (1) and 3 % Ag-doped (2) As_2S_3 films.

As it was mentioned earlier, all the above-considered results were obtained using selective developers containing morpholine, dimethyl sulfoxide and ethanol. Approximately similar non-linear dissolution characteristics were also observed with developers on the base of amylamine. At the same time, developers containing ethylenediamine, diethylamine and dimethylamine, allowing observation of very large γ coefficient for the non-doped As_2S_3 and As_2Se_3 photoresists, did not permit realization of superlinear dissolution characteristics for the Ag-doped As_2S_3 films.

We also studied the process of dissolution of the films after annealing at different temperatures. Typical characteristics for the annealed during 5 min non-doped and 3 % Ag-doped As_2S_3 samples with 2 μm thickness are shown in Fig. 10. With increase of the annealing temperature up to 150°C, which is close to the glass transition temperature, the non-doped As_2S_3 films gradually increased the dissolution time till values in ~ 50 times larger than dissolution time of the non-annealed films. At the same time, the Ag-doped films after annealing to 130°C quickly, super-linearly, increased the dissolution time, which already at 150°C was ~ 700 times

larger than that in the non-annealed films. These results are very similar to the superlinear increase of dissolution time with the growth of irradiation time in the Ag-doped films. One could suspect that the process of interaction of Ag with As_2S_3 glass can proceed not only at irradiation and at increased temperature but also in the darkness at room temperature. However, comparison of as-prepared samples and samples fabricated before one month showed that the time of dissolution of non-irradiated samples practically did not change. These results testify a very good stability of the Ag-doped chalcogenide photoresists.

4. Discussion

The study of different properties and phenomena in the Ag-doped chalcogenide films prepared by coevaporation of Ag with As_2S_3 glass allows concluding that the only unusual effect typical for the doped samples is a strong change in the dissolution process. Use of three irradiation sources: doubled Ne:YAG laser, Hg lamp and solar radiation showed in principal, the same effect – appearance of superlinear dissolution. As it was shown, the Ag concentration and the composition of the developer have essential influence on the dissolution process. Only for narrow range Ag concentrations (1.5-3.5 wt. %) and only in case of morpholine-based and amylamine-based developers application, the nonlinear dissolution characteristics were observed. Annealing of the films was shown to have the effect similar to the increase of irradiation intensity and time: all these factors were accompanied by appearance of non-linear dissolution.

All experimental data allow to think that both irradiation and annealing of Ag-doped films lead to realization of a chemical reaction between Ag and As_2S_3 glass, which is accompanied by delay and later stopping of dissolution. This conclusion agrees with published results of Ag-photodoping [9, 10] and alloying with Ag [18] in chalcogenide glass, which result in cessation of dissolution in alkaline solvents.

We developed a qualitative understanding of the peculiarities of Ag-doped photoresists dissolution basing on the so-called “percolation approach” [19]. In the Ag-doped As_2S_3 film, most of silver particles are in direct contact with As_2S_3 molecules but do not interact with them without light irradiation. Under action of light quanta and also through the annealing process, the Ag-S bonds appear in the As_2S_3 photoresist film and these bonds prevent dissolution of the photoresist in some alkaline developers [20]. Probably, developers based on morpholine and isoamilamine sharply react to appearance of Ag-S bonds. The molecules of the developer, that dissolve the As_2S_3 film, search the places in the chalcogenide film, where the Ag-S bonds are still not created, and the dissolution process is gradually embarrassed. At certain amount of absorbed light quanta (and also at prolong annealing), a great number of Ag-S bonds are already created and the dissolution is essentially embarrassed, when the infinite percolation clusters of structural fragments, containing Ag-S bonds, are formed, what is characterized by the “percolation threshold” [19]. It is clear that this percolation threshold is dependent on the number of absorbed light quanta, meaning, on the light

intensity and irradiation time (and similarly on the annealing time), just as observed in our experiments.

In the films doped with an Ag concentration smaller than 1 %, infinitive percolation clusters could not be formed, and in the films doped by large Ag concentration, such clusters are formed even without light irradiation due to some thermal processes. Here, we want to mention that the percolation approach was already applied for understanding the peculiarities in electrical conductivity and silver diffusion in the Ag-doped chalcogenide glasses [21,22].

Worked out non-linear photoresists have many advantages. Having the characteristics shown in Fig.6, it is possible to select such irradiation time that the working light intensity will correspond to the steep part of the dissolution curves and the harmful image will be in the smooth part of this curve. In this case, the effect of harmful image will be minimized. Nonlinear chalcogenide photoresists, characterized by a very large γ coefficient, allow realization of very high diffraction gratings, while when the linear chalcogenide photoresists is used, the achievable height of the grating is limited in consequence of sufficiently strong light absorption [2-4]. The nonlinear photoresist prevents also the fear of over-etching, which often can exist with linear photoresists. It should be emphasized that all the advantages of nonlinear chalcogenide photoresists were utilized in our experimental photolithographic processes.

5. Conclusions

Inorganic chalcogenide photoresists fabricated by coevaporation of Ag with As₂S₃ glass differ from other photoresists by the nonlinear dissolution characteristics, exhibited by the very quick superlinear growth of dissolution time upon increase of irradiation intensity or irradiation time. This peculiarity is interesting for many different photolithographic processes. In order to understand the reasons of such unusual characteristics, different properties and phenomena in Ag-doped chalcogenide films were investigated in this work. Optical and Raman spectra, photodarkening processes, influence of such factors as Ag concentration, irradiation source, composition of developer and also annealing on the photoresists characteristics were studied. This research showed that neither studied optical spectra nor photodarkening processes in the Ag-doped films have essential distinction from that in the non-doped samples. The difference in the Raman spectra of non-doped and doped films is so small that it does not permit speaking about a serious distinction in the structure. We can conclude that the only serious effect that appeared in the doped samples is the strong change in the dissolution process leading to appearance of the superlinear dissolution.

The superlinear dissolution characteristics are explained by the so-called percolation approach, where formation of Ag-S bonds, appearing and growing in number as a result of irradiation or annealing of the photoresist, at a certain moment practically completely prevents dissolution.

The superlinear photoresists with their giant contrast have many advantages as compared with usual linear photoresists, especially for maskless photolithography when along with the main “working” image on the photoresist, there also exists some spurious optical image which degrades the image contrast.

References

- [1] S. Wong, M. Deubel, F. Perez-Willard, S. John, G. A. Ozin, M. Wegener, G. von Freymann, *Adv. Mater.* **18**, 265 (2006)
- [2] A. Kovalsky, M. Vlcek, H. Jain, A. Fiserova, C. M. Waits, M. Dubey, *J. Non-Cryst. Sol.* **352**, 589. 2006
- [3] N. P. Eisenberg, M. Manevich, A. Arsh, M. Klebanov, V. Lyubin *J. Non-Cryst. Sol.* **352**, 1632 (2006).
- [4] P.S. Even, In *Photoinduced Metastability in Amorphous Semiconductors* Ed. by A.V. Kolobov, Wiley-VCH **365-382**. 1864 (2003).
- [5] R. M. Bryce, H. T. Nguyen, P. Nakeeran, R. G. De Corby, P. K. Dwivedui, C. J. Haugen, J. N. McMullin, S. O. Kasap, *J. Vac. Sci. Technol. A* **22**, 1044 (2004).
- [6] Y. Ruan, W. Li, R. Jarvis, N. Madsen, A. Rode, B. Lutherf-Davies, *Opt. Express*, **12**, 5140 (2004).
- [7] A. Feigel, M. Veinger, B. Sfez, A. Arsh, M. Klebanov, V. Lyubin, *Appl. Phys. Lett* **83**, 4480 (2003).
- [8] A. Zakery, S. R. Elliott, *J. Non-Cryst. Sol.*, **330**, 1 (2003).
- [9] T. Wagner, A. Mackova, V. Perina, E. Rauhala, A. Seppala, S. O. Kasap, M. Frumar, Mir. Vlcek, Mil. Vlcek, *J. Non-Cryst. Sol.* **299**, 1028 (2002).
- [10] L. Russo, M. Vlcek, H. Jain, *Glass Technol.* **46**, 94. (2005).
- [11] V. Lyubin, A. Arsh, M. Klebanov, R. Dror, B. Sfez, *Appl. Phys. Lett*, **2008**, 92,
- [12] R. Swanepoel, *J. Phys. E* **16**, 1214 (1983).
- [13] M. S. Chang, T. W. Hou, *Thin Solid Films* **55**, 463 (1978).
- [14] C. W. Slinger, A. Zakery, P. J. S. Ewen, A. E. Owen, *Appl. Opt.*, **31**, 2490 (1992).
- [15] S. A. Solin, G. N. Papatheodoru, *Phys. Rev. B* **15**, 2084 (1977).
- [16] A. V. Stronski, M. Vlcek, A. I. Stetsun, A. Sklenar, P. E. Shepeliavyi, *Semiconductor Physics, Quantum Electronics & Optoelectronics* **2**, 63 (1999).
- [17] D. Y. Choi, S. Madden, A. Rode, R. Wang, B. Luther-Davies *J. Appl. Phys.* **102**, 083532 (2007).
- [18] N. Yoshida, K. Tanaka, *J. Appl. Phys* **78**, 1745 (1995).
- [19] S. Kirkpatrick, *Rev. Mod. Phys.* **45**, 574 (1973).
- [20] A. V. Kolobov, S. R. Elliott, *Adv. Phys.*, **40**, 625 (1991).
- [21] E. Bychkov, V. Tsegelnik, Yu. Vlasov, A. Pradel, M. Ribes, *J. Non-Cryst. Sol.* **208**, 1 (1996).
- [22] E. Bychkov, D.L. Price, *Solid State Ionics* **136-137**, 1041 (2000).

