НОВЫЕ РЕЗУЛЬТАТЫ ФУНДАМЕНТАЛЬНЫХ И ПРИКЛАДНЫХ ИССЛЕДОВАНИЙ ХАЛЬКОГЕНИДНЫХ СТЕКЛООБРАЗНЫХ ПОЛУПРОВОДНИКОВ

Статья является обзором последних исследований фотоиндуцированных явлений в халькогенидных стеклообразных пленках, выполненных в Университете Бен-Гуриона (Израиль).

1. Introduction

One of us (V.L.) had opportunity and pleasure to collaborate for a large period of time with G. A. Bordovsky in investigation of chalcogenide glassy semiconductors, and it is great honor for us to present our recent results in the book, which is dedicated to Professor G. A. Bordovsky on ocassion of his 65^{th} birthdays.

Chalcogenide glassy semiconductors (ChGS) and particularly optical, photoelectrical and photoinduced phenomena in these disordered materials continue to attract attention of researchers and engineers in many countries. Study of such phenomena as optical memory, photoinduced reversible crystallization-amorphiszation, photoinduced structural transformations, photoinduced anisotropy, photodoping by different metals resulted in obtaining of many new interesting fundamental and applied results. Simultaneously several new phenomena were discovered and investigated: optical non-linearity, poling effect and higher order optical harmonics generation, luminescence in chalcogenide glasses doped by the rare-earth elements, peculiarities of photoelectrical and optical processes in the metal-chalcogenide glasses. All these phenomena are interesting both for the physics of amorphous solids and as the basis for the development of new devices of modern electro-optics.

In this paper we summarize some results obtained recently in the laboratory of amorphous semiconductors of the Ben-Gurion University of the Negev in Israel when studying several of the above-mentioned optical and photoinduced phenomena. We also consider some new applications of ChGS films.

2. Photoinduced structural transformations

In our research we showed that strong increase of photosensitivity could be achieved when structural transformations in ChGS are induced by short intense laser pulses [1]. Comparison of the effects of single ArF laser pulse (16 ns, 0.5-4.5 mJ) and CW He-Ne laser radiation on transmission of As-Se film is demonstrated in Fig. 1. It

is seen that the sensitivity of photodarkening in the former case is about 1500 times larger. Similar results were obtained when short intense pulses (5 ns, 3-5 mJ) of Nd:YAG laser were used for the As-S films and KrF laser pulses (16 ns, 15 mJ) — for the As-Se-Te films. All properties of photodarkened film areas did not depend on the mode of excitation, pulse or CW.

Study of dynamic characteristics of photostructural transformations indicated that strong increase of photosensitivity following short intense light pulses is due to a multi-photon effect that eases the process of structural rearrangement. If two photons are absorbed close to each other and weaken or break the neighboring interatomic bonds of the chalcogenide glass, the process of structural rearrangement proceeds with much larger probability but this process can be realized only at sufficiently large writing beam fluences [2]. These results allow us to claim that ChGS films with their high optical resolution are the very prospective materials for pulsed holography, pulsed photorecording and pulsed photolithography.

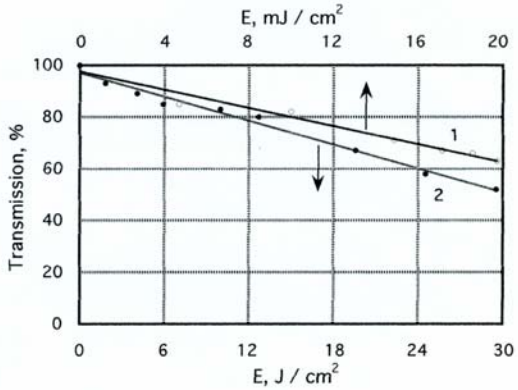

Fig. 1. Change of transmission of ~ 0.4 μm As-Se film as a function of radiation of ulsed ArF laser (1) and CW He-Ne laser (2)

3. Photoinduced anisotropy

All previous studies of photoinduced anisotropy in ChGS demonstrated the effect of *optical* anisotropy [3, 4]. In our recent investigations we demonstrated that photoinduced optical anisotropy is accompanied by the photoinduced anisotropy of photoconductivity [5]. When the $As_{50}Se_{50}$ sample with two parallel electrodes was irradiated by a non-polarized He-Ne laser beam, we detected appearance and subsequent saturation of photocurrent. Following irradiation by linearly polarized light with an electric vector E either parallel (Ex), or orthogonal (Ey) to electrodes resulted in appearance of anisotropy of photocurrent (Fig. 2). To the best of our knowledge, this is the first reported case of the photoinduced *electrical* anisotropy observation in the ChGS.

Analyzing the obtained results, we conclude that the observed anisotropy of photoconductivity is due to anisotropy of carriers mobility. The obtained data indicate that the microanisotropic species, responsible for optical anisotropy [3, 4], affect not

only the light absorption process but also the process of transport of non-equilibrium charge carriers. While normally these microanisotropic species are oriented randomly that results in the isotropic photoconductivity, irradiation with linearly polarized light results in alignment of these species and respective anisotropic photoconductivity.

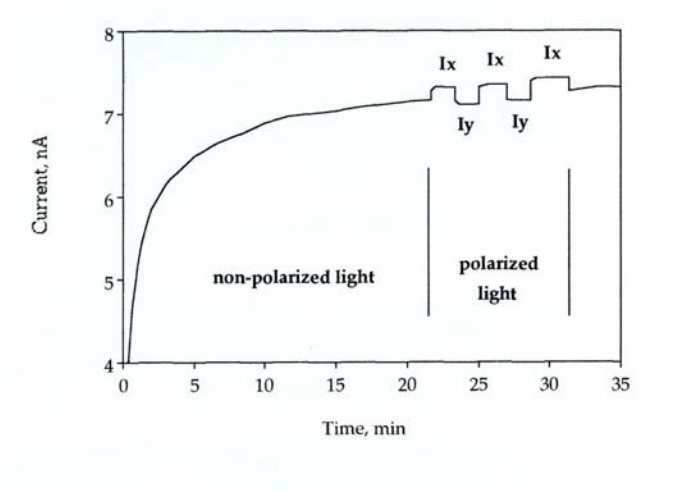

Fig. 2. Kinetics of photocurrent following the change of the polarization state E of the inducing beam of He-Ne laser in a two-electrodes AsSe sample

4. Polarization-dependent anisotropic photocrystallization

Our study of the polarized light interaction with ChGS films resulted in revealing of new peculiarities in the phenomenon of photocrystallization of amorphous films. This phenomenon was discovered in 1968 [6] and then was studied already during more than 30 years. We found that the polarization state of the excited light influences the photocrystalization process and the properties of crystallized samples [7, 8]. Irradiation of glassy $Se_{70}Ag_{15}I_{15}$, Se and $Se_{80}Te_{20}$ films with linearly–polarized He-Ne- and Ar^+- laser light was shown to result in formation of polycrystalline films with strong optical anisotropy (dichroism), the sign of which is determined by the direction of the electrical vector of light. As it is seen from Fig. 3, the photoinduced dichroism excited by the He-Ne laser light in the $Se_{70}Ag_{15}I_{15}$ film at a constant direction of polarization vector achieves very large values of about 15–18%. The sign of the final dichroism always was determined by the direction of the exciting light polarization vector. Final dichroism was stable and did not relax in the darkness. Annealing of irradiated films at glass transition temperature (55 ºC) and at 80-90 ºC for several hours did not lead to a destruction of photoinduced dichroism. Thus, all characteristics of PA in treated Se-Ag-I, $Se_{80}Te_{20}$ and a-Se films were different from those in films studied previously. The results obtained (unusual kinetics, another sign and large value of photoinduced dichroism, absence of relaxation and thermal destruction) permitted us to assume that we deal with photoinduced photocrystallization process. This assumption was confirmed by the direct structural investigations including optical microscopy, electron microscopy and X-ray diffraction study [7, 8]. Thus, we observed the polarization-dependent laser-induced anisotropic photocrystallization of Se-Ag-I, $Se_{80}Te_{20}$ and a-Se films. It is necessary to say that the same effect of polari-

zation-dependent laser-induced photocrystallization of a-Se films was revealed approximately simultaneously and completely independently in two other groups [9, 10].

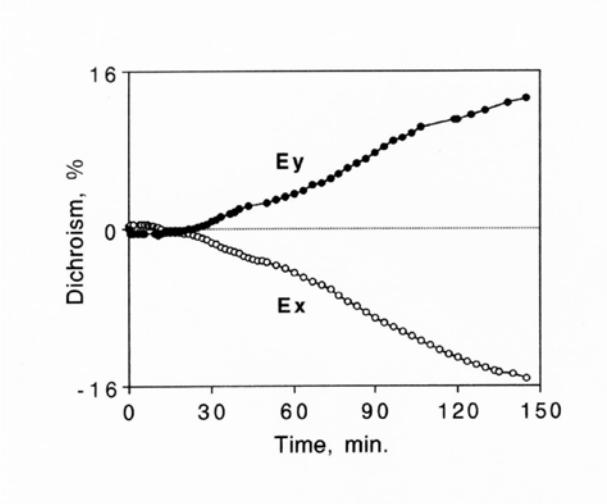

Fig. 3. Kinetics of dichroism generation in treated $Se_{70}Ag_{15}I_{15}$ film induced by a linearly polarized He-Ne laser beam with horizontal (Ex) and vertical (Ey) directions of the electrical vector

5. Photoluminescence in the rare-earth-doped chalcogenide glassy films

Chalcogenide glasses doped with (RE) ions, e. g. Er^+, Nd^+, Dy^+ or Pr^+ are attractive materials for a wide range of applications in fiber lasers and fiber amplifiers operating in the 1.2–1.7 μm wavelength range [11, 12]. The results obtained at study of photoluminescence of RE-doped bulk chalcogenide glasses were reported in papers [13, 14].

In many cases of practical application, it is necessary to have the RE-doped thin chalcogenide films with efficient I.R. luminescence and this task encounters the problem of large difference in evaporation rates of chalcogenide glasses and rare-earths, which does not allow to apply usual thermal evaporation technique. We proposed a new simple method for the RE-doped films preparation, based on coevaporation in vacuum of the chalcogenide glass and the RE containing material [15].

Thin Er- and Nd-doped As_2S_3 and As_2Se_3 films were prepared by thermal coevaporation of starting crushed glassy chalcogenide material from quarts crucible and Er_2S_3 or Nd_2S_3 powder from a tungsten boat onto Corning-glass substrate in vacuum of (1–3) x 10^{-6} Torr. Keeping the constant rate of RE-sulfide evaporation, we varied the rate of chalcogenide glass evaporation and fabricated the samples with different Er or Nd concentration in the range of 0.3–1.8 wt%.

All RE-doped chalcogenide films kept ability to have the photostructural transformations which are displayed in photodarkening, photoresist effect (the ratio of dissolution rates for non-irradiated and irradiated areas has values till ~50).

The PL spectra with typical Er-ion emission for two Er-doped chalcogenide samples are shown in Fig. 4. Linear PL intensity dependence on the exciting laser beam intensity was observed. The PL spectra in Nd-doped As_2S_3 films with concentration of Nd in the range of 0.4–1.6 wt% indicated two maxima of luminescence at

~1080 nm and ~900 nm, as it is demonstrated in Fig. 5. Such spectra are typical for photoluminescence of very different Nd-doped solids. Especially significant luminescence was observed at intermediate concentration 0.8–1.3 wt%, at larger Nd concentration the luminescence intensity was smaller.

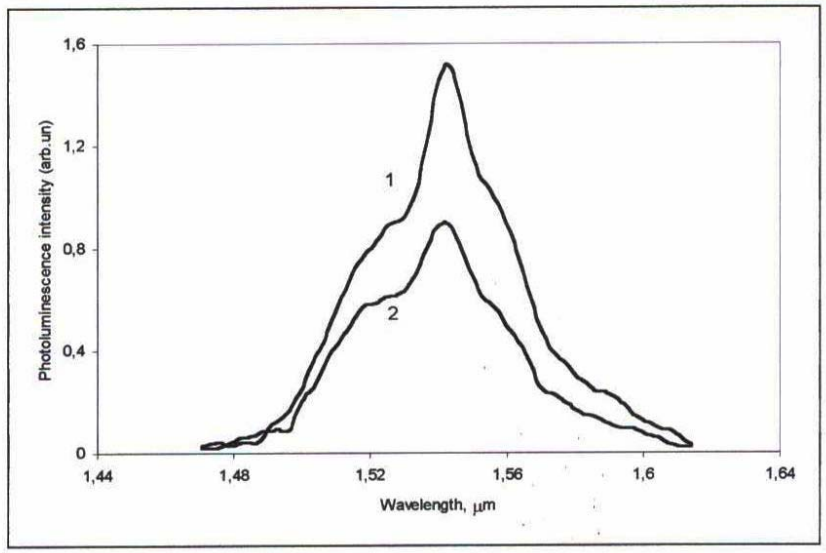

Fig. 4. Photoluminescence spectra in Er-doped As_2S_3 (1) and As_2Se_3 (2) films excited by 0.1 W/cm^2, 515 nm Ar-laser beam

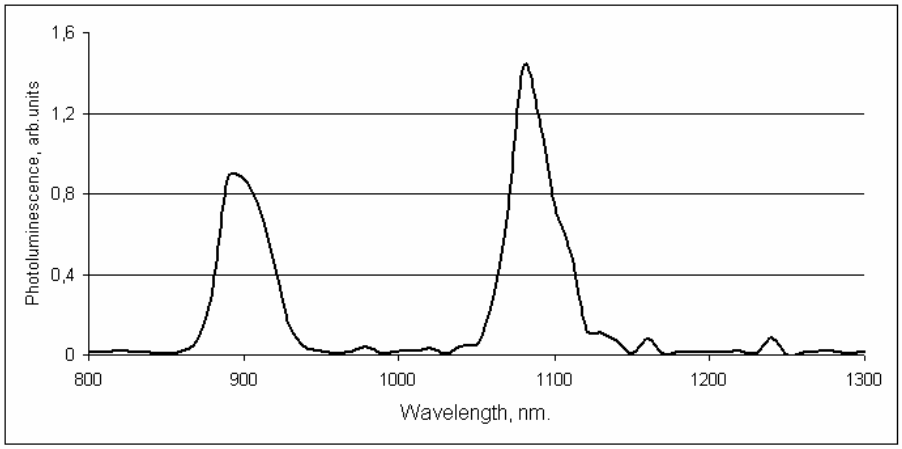

Fig. 5. Typical photoluminescence spectrum in Nd-doped As_2S_3 films excited by 0.02 W/cm^2, 488 nm Ar-laser beam

6. New applications of ChGS films

The ChGS photoresists were shown previously to have many interesting properties. They are sensitive in wide spectral range. Transition from positive to negative lithographic process with the same photoresist can be performed very easily by

changing the composition of the developer. All chalcogenide photoresists are characterized by extremely high resolution better than 0.1 μm, good optical transparency in the 0.8–12.0 μm range and high refractive index values between 2.3 and 3.5. Due to these properties we succeeded to find new applications of chalcogenide photoresists.

6.1. Microlens arrays

Microlens and microlens arrays can be found in an increasing number of optoelectronic applications, such as optical communication and computing, CCD cameras, faxes, imaging systems and IR technology. We proposed new technology for fabrication of IR microlens arrays, based on the use of chalcogenide glasses that are simultaneously effective photoresists and good I.R. optical materials.

The method proposed is essentially the direct one-step formation of a 3D microlens array using dependence of the etching rate on the illumination intensity of chalcogenide photoresists. Both spherical and cylindrical I.R. microlens arrays were successfully fabricated using As-S and As-Se photoresists [16, 17].

6.2. Micro-prism arrays

Microprisms and microprism arrays are interesting and important elements for a number of purposes such as beam coupling or combination, for integrated planar optical interconnections where they are capable of realizing large coupling angles at sufficiently high efficiencies. In the fabrication of microprisms and microprism arrays the specialists usually apply complicated and expensive technology based on anisotropic reactive ion etching processes [18].

We propose a new technology for fabrication of microprism arrays for I.R. light, which has the potential to eliminate the ion etching process [19]. The method proposed is similar to the above-considered method for fabrication of I.R. micro-lens arrays. In the case of micro-prism fabrication it is very important to have very soft contrast characteristics (dependence of remaining photoresist thickness on the dose of irradiation) of the photolithographic process, which are characterized by a long quasi-linear section. In the developed technology, we used three-component As-S-Se chalcogenide photoresists and new efficient amine-based selective developers, which together allowed to realize the necessary soft contrast characteristics of the photolithographic process using an Xe- source of light.

Using different gray scale photomasks, microprisms with wide variation of their geometric parameters were obtained. One of such arrays with microprism base width 5μm is represented in Fig. 6. As it was mentioned above, chalcogenide glasses are characterized by high values of refractive index in the range of 2.3–3.5 and therefore the chalcogenide microprisms can be used for coupling of I.R. light beams into optical wave-guides with high refractive index, particularly, into wave-guides produced from chalcogenide glasses [20].

6.3. Photonic-band-gap structures

Photonic-band-gap crystals have been the object of intense activity. We fabricated the three-dimensional photonic-band-gap structures on the base of the As_2S_3, mAs_2S_3 x nAs_2Se_3 and As-Se-Te films [21]. These structures contained a layer-by-layer structures, in which each layer was formed by vacuum evaporation of 0.3 μm $AsSeTe_{0.1}$ film, used as a negative photoresist and as an optical material with high refractive index. Then we performed writing of a holographic pattern by two-beam interference and etching of the non-illuminated parts. The grating obtained by this procedure was planarized using spin-coated organic Shipley`s photoresist, and the next

layer is formed on the previous one. The direction of the grating in the second layer is perpendicular to the first one. In subsequent odd layers, the direction is parallel to the first one, and in the even layers — to the second. In addition, the half period phase shift exists between each two nearest parallel layers. Finally, the organic photoresist can be washed out by acetone, remaining the $AsSeTe_{0.1}$ photonic-band-gap structure. We succeeded also to realize three-dimensional and two-dimensional photonic crystals using the RE-doped As_2S_3 films. These crystals were characterized by strong photoluminescence. An example of three-dimensional photonic crystal is shown in Fig. 7.

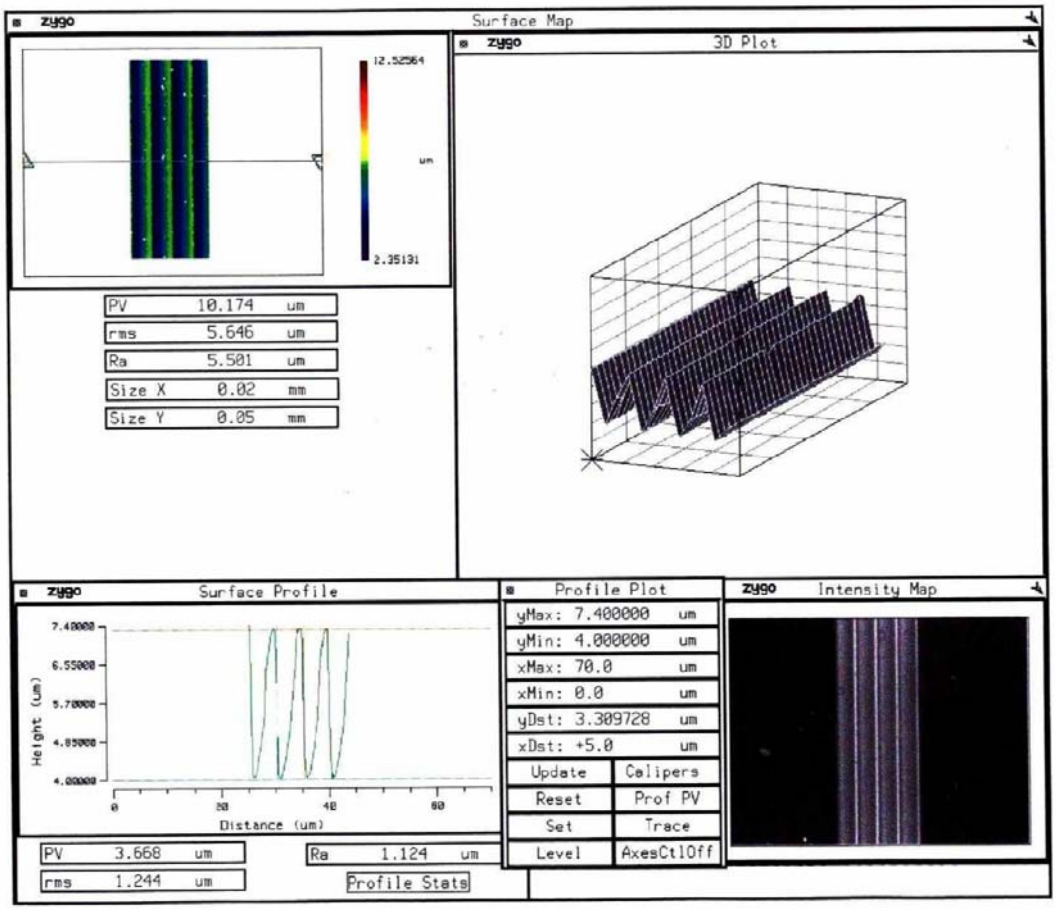

Fig. 6. Microprism array with microprism base width 5μm

7. Conclusion

Results considered in the present review paper demonstrate that the ChGS continue to be the very interesting and promising non-crystalline materials. They display different new interesting physical phenomena, which are not observed in other semiconductor materials. ChGS open new prospects in development of different efficient electro-optical and micro-optical devices. We can hope that in near future the ChGS will allow to develop new efficient devices for optical communication systems.

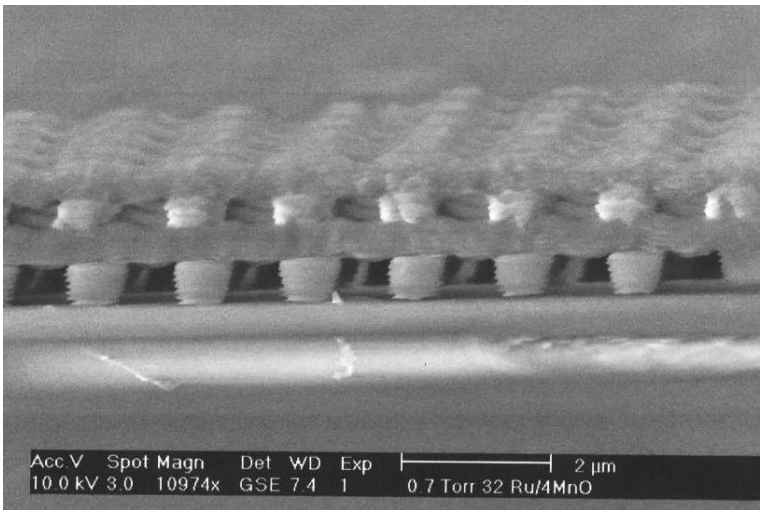

Fig. 7. The scanning electron microscope image
of the four layer As_2S_3 three-dimensional layer-by-layer photonic crystal

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NEW RESULTS IN FUNDAMENTAL AND APPLIED STUDY OF CHALCOGENIDE GLASSY SEMICONDUCTORS

This short paper contains review of recent results obtained during the study of photoinduced phenomena in chalcogenide glassy films in the laboratory of amorphous semiconductors of the Ben-Gurion University of the Negev in Israel.