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Ovshinsky Prize Lecture

CHALCOGENIDE GLASSES AS MULTIFUNCTIONAL PHOTONIC MATERIALS

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First of all I would like to thank my colleagues from the Forum of Chalcogeniders and especially to thank Prof. Stanford R. Ovshinsky for the great honor offered to me: his prestigious Prize for 2005. Stanford Ovshinsky is a great personality of our times, who combines successfully the ability of engineer with the open mind of the scientist. He remarked as early as 1960 the importance of the new group of materials, the chalcogenide glasses (ChG), that are not only excellent materials for the physics of non-crystalline semiconductors but also materials with wide applications in optoelectronics, electronics and informatics.

I want to start my lecture by remembering the old times when I have had the occasion to work in the Laboratory of Professor Boris Kolomiets in former Leningrad (Russian Federation). The famous team working under the leadership of Kolomiets was for me not only a rich source of ideas and example of hard and efficient work in chalcogenides, but, also, a school of high intellectual and moral qualities. Along the time I collaborated with the scientists originated from this school: V. M. Liubin, T. N. Mamontova, T. F. Mazets, E. A. Lebedev, C. Tsendin and A. V. Kolobov.

Other great personalities in the world, stimulated me in the study of non-crystalline materials, including the chalcogenides: Sir Nevill Mott, Nobel Prize for Physics (1977), who highly appreciated the contributions of B. T. Kolomiets, Prof. R. Grigorovici with outstanding discoveries related to the structure of non-crystalline semiconductors, J. Tauc whose "Tauc tail" is now a common concept in amorphous semiconductors, A. F. Ioffe and Prof. A. R. Regel who made important discoveries in the physics of ChG. It is a pleasure to mention that, now, the efforts of Prof. R. Grigorovici in Bucharest are continued with great success by Mihai Popescu. The community of chalcogenide people is thankful for his activity in the field of ChG research and for stimulating the the publication of the research results in the frame of Journal of Optoelectronics and Advanced Materials, Chalcogenide Letters, Journal and Ovonic Research, and specialized books. Many papers that reported important advances in non-crystalline chalcogenide science and applications have been published in the last years in these journals or posted on the Web site of the chalcogenide people (http://www.chalcogen.infim.ro) [1-17].

I would like to mention that nowadays the development of the civilization is characterized by a fast increase of the amount of information, which stimulated the development of telecommunication technologies on optical basis, using laser as source of generation of informational signals, the optical fibers as media for transport of optical signals at long distances without large losses and the optical processors which process at the same time a high amount of information with high speed, the media of optical information storage with practically unlimited capacity of storage, with ultra-high spatial resolution. The photonic elements of our technical civilization have as targets the telecommunication systems, the optical sensors of ultra high sensitivity used in robotics, as well as the detection of the thermal energy and transmission systems throughout optical fibers with large applications in medicine.

Up to day it does not exist an universal material, as silicon in microelectronics, which would satisfy all requirements of the photonics. In different laboratories around the world, various

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materials are studied, intended to cover a large number of technical possibilities. Among the groups of materials under focusing for optoelectronic applications, a special place is occupied by the non-crystalline materials, based on chalcogenides and polymers with special properties. Namely, these materials are studied in the Center of Optoelectronics of the Institute of Applied Physics of the Academy of Sciences of Moldova in Chishinau, using a wide range of compositions, various fabrication technologies for bulk materials, thin films, planar and cylindrical guides, optical fibers. Many results have been published in books [18, 19].

In my lecture, I want to discuss the last development of the research in chalcogenides, carried out in Chishinau under my leadership. The following points will be reached:

1. Registration media and holographic information technologies
2. Photo-induced absorption.
3. Photoluminescence and phenomenon of amplification of light in ChG fibers.
4. New photonic materials on the basis of nano-composites polymer-ChG.
5. Registration media and holographic information technologies

As it is well known, the thin ChG layers exhibit photostructural properties, of high importance for optical information recording and for holographic technology. High-quality recording materials must satisfy definite requirements as: high sensitivity, simple chemical development, good spatial-frequency response, high diffraction-efficiency level, high signal-to-noise ratio, high stability of the holographic materials, the possibility to use the same films in the process of application of both methods of photo- and electron-beam lithography. These requirements are very often contradictory. That is why it is necessary to find new materials that satisfy as much as possible the above mentioned requirements, and to diversify the methods for information recording. It is important to observe that the influence of the electric field in the process of formation of holographic diffraction lattices in chalcogenide materials is of interest. This effect was in our attention in the last years.

Thin simple film structure, as e.g. metal-ChG-metal and metal-ChG-ion electrode was considered as objects of study (the ionic electrode was created by using a xerographic method). Compositions from the system As –S-Se-Ge, because their photo-structural properties are well expressed [20, 22].

Three types of recording phenomena in chalcogenides are known:

(a) electro-diffusion of ions of electrode material;

(b) thermo-plastic modification of ChG;

(c) changing of space optical properties of ChG due to the accumulating of non equilibrium carriers on localized states.

I shall mention only the main peculiarities of these phenomena:

(a). There were observed electro-stimulated chemical transformations (ESCT) in metal - ChG-metal structures due to interaction of electrode (Al) with ChG . When positive polarity is applied to Al electrode we are dealing with electro-diffusion of Al ions and with transformation of Al electrode in Al_2O_3. It was shown that the regions of samples exposed to light, if subjected to ESCT, are dissolved much faster in alkaline solutions than the unexposed ones. The process can be applied in electrically controlled photolithography with high resolution capability (more than 1000 mm-1)[23, 24].

(b). Under the simultaneous action of the applied electric field and light to thin film structures metal -ChG- -metal occurs a strong heating of the GhG up to T_g temperature. The sharp increase of the density of the photocurrent in the illuminated pars leads to the creation of micro-deformations that lead to the change of transmittance and reflection, which are preserved after switching off the current. This phenomenon was named *effect of electro-stimulated deformation of the surface (ESDS)* and it is similar to the photo thermo plastic [25]. Because the deformation size is

very small and since they are strongly oriented, this process can be used for the registration of the holographic information.

The amplification of the effect has been made by the photo injection in film from different crystals (InP, GaP, In_2S_3, In_2Se_3). By changing the polarity of the applied field it is possible to create the conditions of involving both processes, (a) and (b), in the registration (Fig.1) [25].

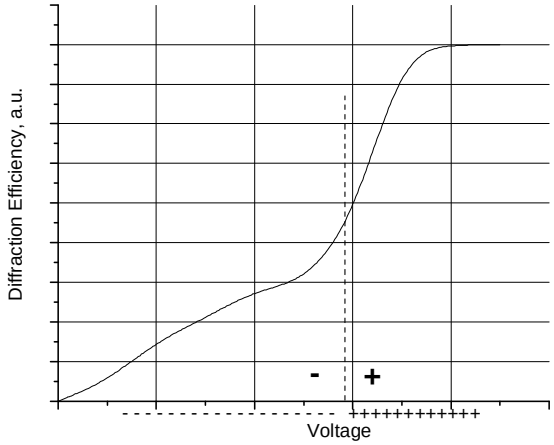


Fig. 1. The curve of the diffraction efficiency of the micro-hologram, recorded on the Al-In_2S_3/As_2Se_3-Al, when voltage impulses of negative and positive polarity are applied.

(c). The study of the possibility of optical information recording when the electrode material does not interact with ChG is, also, important. In this case we must take into account the electronic mechanisms of recording.

As expected [26], as a result of illumination of ChG samples, non-equilibrium carriers of charge are produced and they diffuse away from the positions of high concentration, where they are generated. A fraction of non-equilibrium carriers is trapped on the localization energy levels, thus resulting in the formation of an inhomogeneous space-charge distribution. They are maintained for a time after removing the light. This residual spatial charge creates an internal electrical field that modulates the local refractive index of the material by virtue of the electro-optical effect. The applied external electric field modifies the optical properties of the material due to the distortion of the distribution of trapped charge. Thus, it is promoted the increase of the extent of division of an internal spatial charge that should be manifested in increasing value of refraction index. In such conditions the selective etching leads to the formation of more relief structures and to growth of diffraction efficiency of gratings structures [26].

As a result of applying an electric field to the structures metal-ChG-ion electrode in the regime of corona discharge, many recording parameters are improved.

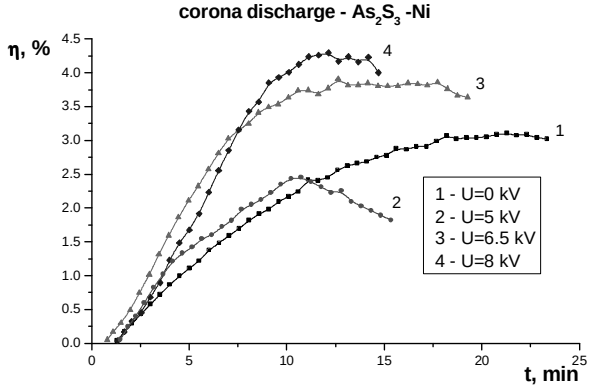
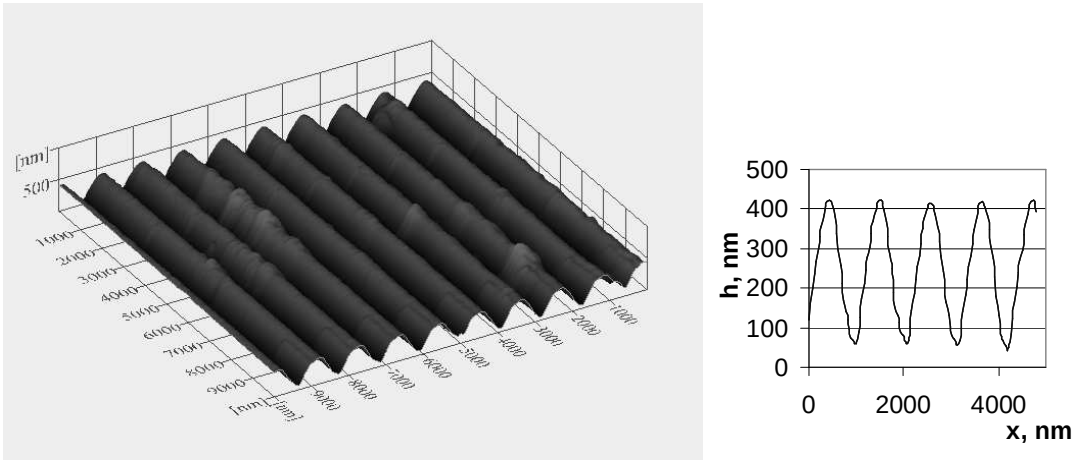


Fig 2. Diffraction efficiency dependence on recording time.

As it is seen from Fig. 2, the application of an electric field leads to the increase of the diffraction efficiency by 2.5-3.5 times. Other optical parameters are increased, too, for example the photosensitivity of ChG is raised by 1.5-2 times, the dynamic range is expanded by 1.5 times, the time necessary for achievement of actual value of diffraction efficiency is reduced by 2, and, finally, after etching and metallization the diffraction efficiency increases by 50-200%.

The diffraction gratings (DG) on the surface was studied by Atomic-Force Microscopy (Fig. 3, a) without applied field and b) with applied field given by a corona discharge. As it is seen, the profile of the gratings can be approximated, with a high degree of accuracy, by a cycloid (the gratings has about 2000 mm^{-1}) (Fig. 3a). At the same time the samples obtained in the conditions of applied electric field have the profile closer to sinusoidal wave (Fig.3b). By comparison of these data it was also established, that the application of an electric field leads to an increase in the degree of regularity and depth of the relief by 25-30 %. Thus the profile becomes quasi- sinusoidal.



a b

Fig. 3. Topography and the shape of the structure of stroke holographic diffraction lattices got in an applied electric field.

The above mentioned results demonstrate the possibility to elaborate on the basis of the phenomena observed in ChG materials, of new electrically controlled recording media with high performance for the duplication of holographic matrix, for the fabrication of nano-structures and other optical elements.

There are several mechanisms that explain the photo-induced absorption in ChG. I shall discuss only the pure electronic processes. The largest application has the model of multiple carrier trapping in localized states (Fig. 4), developed in [27-34].

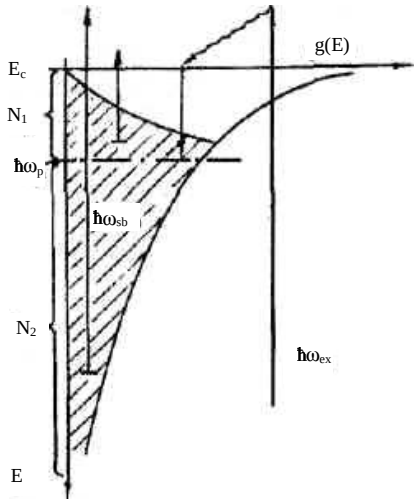


Fig. 4. The model of localized states in the forbidden gap of amorphous materials.

When ChG are excited by light of energy $h\nu > E_g$, non-equilibrium carriers appear in the empty bands. Very quickly they are captured by the tail states. The probing light with energy $h\nu < E_g$ excites the trapped carriers in the band of localized states. This leads to photo-induced absorption due to pure electron processes. In order to observe better the small changes in photo-induced absorption we used ChG optical fibers that enabled us to enlarge the optical path. In such conditions the photo-induced absorption is caused by lateral excitation of fibers by light from the region $h\nu > E_g$. *I must mention that very large signals are observed* even for $h\nu < E_g$, due to longer optical path in the fibers [29,30, 35,36].

When the lateral surface of the fiber is illuminated with continuous band gap light, the intensity of the probing light at the output of the fiber decreases from its initial value (in the dark) because of the photo-induced absorption.

The qualitative analysis of the experimental results in terms of multiple trapping enabled us to evaluate some parameters of localized states distribution and career transport [36]. For example, it was possible to evaluate some parameters which are very difficult to obtain from direct experiments, such as:

- the characteristic energy of the distribution of localized states, E_o*: 0.26 eV;*
- the temperature dependence of hole drift mobility in As_2S_3;
- the recombination radius

If the intensity of light pumping is very high, a photo-induced non-linear absorption can be observed in ChG. Some mechanisms can be advanced. First of all it is necessary to mention the mechanism with the participation of non-equilibrium localized phonons [31-33].

The excitation of the non-equilibrium carriers in ChG with the energy of photons $h\nu > E_g$ leads to the appearance of hot electrons and holes. Their thermalization in the non-crystalline systems is accompanied by the generation of non-equilibrium localized phonons (fractons).

The phonons with the wavelength of the order of magnitude of the modulation length of the random potential in the ChG drastically modify the form of the potential, which modulates the bottom of the conduction band and the top of the valence band of the ChG [33].

In such a way the non-equilibrium localized phonons open a new channel of the inter-band light absorption. The participation of the fractons in photo- induced absorption in ChG leads to a hysteresis form of the dependence $I=f(I_o)$. I have already shown, in collaboration with the group of professor Mario Bertolotti, that this type of photo-induced non-linear absorption appears even in femto second region [34, 37].

Optical fibers amplifiers are the key devices for increasing the transmission distance, speed and capacity of optical communication systems. Optical fiber amplifiers based on rare-earth doped chalcogenide glasses are potential candidates for the communication systems and satisfy all the main requirements: high output power and low noise, a broad gain spectrum, high reliability, low costs and compactness [38, 39].

The most promising candidates for optoelectronics applications are glassy As_2S_3 and As_2Se_3. This is due to their high transmission in the infrared (up to 10 μm), high refractive index ($n \approx 2.4$) and low phonon energy. The band gap of As_2S_3 lies in the visible region of the spectrum ($E_g \approx 2.4$ eV), and, thus, the optical transitions involving the conduction bands and edge tail states overlap with some absorption/emission bands due to the discrete levels of the rare-earth ions[40]. For this reason, the photon energy absorbed in the broad band region in rare earth doped As_2S_3 glasses is partially transferred to rare earth ions, and this leads to the enhancement of the efficiency of luminescence. This is an important effect for applications in fiber optics amplifiers operating at 1.3 μm and 1.5 μm telecommunication windows.

The fluorescence spectrum of As_2S_3 bulk glass samples doped with different rare-earth elements is shown in Fig. 5 [41]. Two quite smooth luminescence bands located around 1.3 μm and 1.5 μm can be observed.

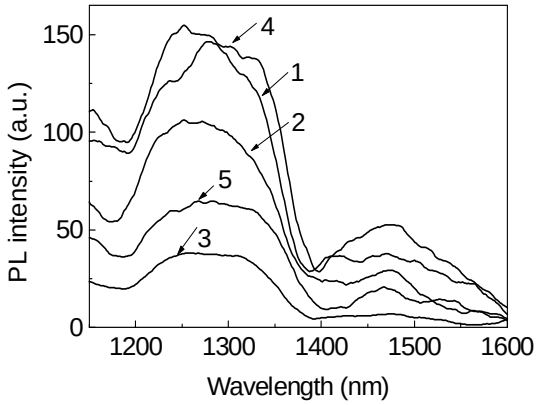


Fig. 5. The luminescence spectra of As_2S_3+0.15 at.% Pr (1), As_2S_3+0.25 at.% Pr (2), As_2S_3+0.5 at.% Pr (3), As_2S_3+0.5 at.% Dy (4), and As_2S_3+0.1 at.% Er (5). The excitation light source was a LED (λ=0.95 μm).

When optical fiber sample is excited with a light beam of wavelength 0.808 μm, the luminescence spectra exhibit a narrow band positioned at approximately 1.6 μm (Fig. 6). The fluorescence at 1.6 μm is associated with the $(^3F_3, ^3F_4) \rightarrow ^3H_4$ transitions [41].

In the case of excitation with the laser beam of wavelength 1.02 μm, the sulphide fibers doped with Pr^{3+} ions show a luminescence band located at around 1.35 μm [42, 43].

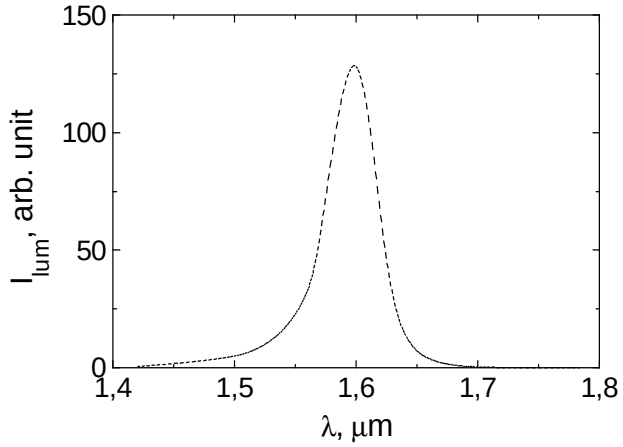


Fig. 6. The spectral distribution of the photoluminescence in As_2S_3 chalcogenide glass fibers doped with 0.5% Pr. The excitation light source was a laser diode (λ = 0.808 μm).

Therefore, the experimental results of photoluminescence in arsenic sulfide glasses and optical fibers doped with rare-earth elements (Pr^{3+}, Sm^{3+}, Er^{3+} and Dy^{3+}) convincingly confirmed that chalcogenide glasses are potential materials for fiber optic amplifiers operating at 1.3 and 1.5 μm telecommunication windows.

As it was shown by many authors [see for example 44], the polymers manifest photo-chemical transformations that allows to use them for optical information recording. Significant photo-structural modifications are characteristics for ChG. At the same time polymers and ChG have very different physic-chemical and optical properties being transparent and having photosensitivity in different spectral range. For optimization of the sensitive parameters, simplification of the technology of fabrication, improving the stability of the registration media, solving problems related to ecological outputs, it is reasonable to combine the properties of these two groups of materials by getting nano-composites from polymers and ChG. With this purpose films from polyvinyl alcohol

polymer with added arsenic sulfide and sulphur have been prepared [44]. The concentration of As_2S_3 has been varied from 1% to 20% wt. of polymer. The thickness of the films was situated at about 3 μm. The transmission spectra in the visible and infrared region are presented in the Figs. 7, 8 for nano-composites polymer- As_2S_3.

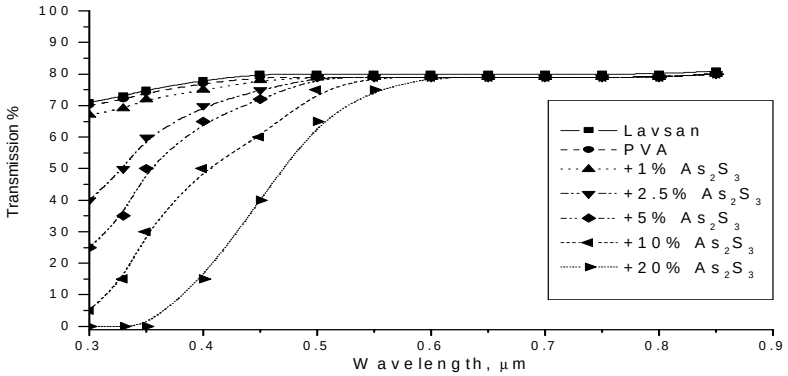


Fig. 7. Transmission spectra of the composition: PVA with various concentration of As_2S_3.

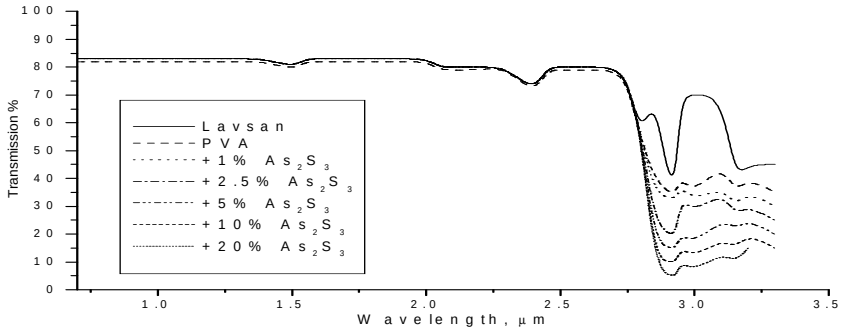


Fig. 8. Transmission spectra of the composition: PVA with various concentration of As_2S_3

Spectra are similar to those of As_2S_3 [see for example 45, 46]. At the same time, with the decrease of the As_2S_3 component in the polymer composition the absorption edge is shifted towards the short wavelength side (Fig. 7). On the long wavelength side the transparency "window" (Fig. 8) is limited to 2.9 μm by the absorption band, which increases by increasing the As_2S_3 content in the polymer composition. In the opinion of the authors of [47] this is related to the presence in the samples of water molecules. It is very important to note that the irradiation of films, made of nano-composites polymer-arsenic sulfide (As_2S_3), by ultra-violet light (incident energy E=10-20 mW/cm^2), leads to the appearance of a new band of absorption in the range of 0.65-0.68 μm [Fig. 9].

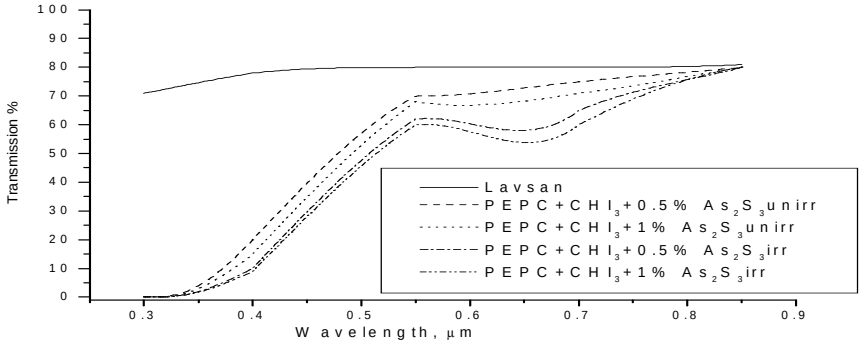


Fig. 9. The transmission spectra of the composition: PEPC+CHI_3 with adding As_2S_3 before and after irradiation.

The importance of this feature is related to the possibility to move the spectral range of photosensitivity of nano-composites from ultraviolet to red one, a very convenient wavelength. Similar results have been obtained on the films made of nano-composites polymer-sulphur (S) [44].

On the basis of the study regarding the influence of the electric field on the optical properties, including the processes of formation of holographic diffraction lattices in ChG, there were developed new electrically controlled recording media with performant parameters for duplication of holographic matrix, for fabricating nano-structures and other optical elements. Metal-chalcogenides composites were prepared [48] and photo-resist manipulation techniques were developed [49,50].

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