

Dedicated to Acad. Prof. Dr. Margareta Giurgea with the occasion of her 90-th anniversary

DISORDERED CHALCOGENIDE OPTOELECTRONIC MATERIALS: PHENOMENA AND APPLICATIONS

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The glassy, amorphous and disordered chalcogenide materials, important for optoelectronic applications, are discussed. The main optical and optoelectronic phenomena, specific to these materials are shown, and the applications based on these phenomena are evidenced.

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1. Introduction

The modern technological era started with the invention of the transistor in 1947, when the solid state electronics was born. From that date we have been the witnesses of a rapid development of science and technology based firstly on germanium, then on silicon, and later on GaAs crystalline materials.

The necessity to save weight and size, and to improve the speed in the function of the devices, stimulated an intense research activity with the purpose to reach the nanometer size field. In the same time the worldwide interest was moved from electronic to more complex optoelectronic applications.

Taking into account these big tasks of the 21-st century, the class of materials must be enlarged. New materials with new properties must be prepared. It is remarkable, that, starting with '60 a new competitor appeared on the market of materials with implications in optics, electronics and optoelectronics: the disordered, amorphous or glassy materials.

The science of glass developed step by step. New classes of materials have been discovered. The first one was the large class of chalcogenides, materials that contain one or more chalcogen elements: sulphur, selenium, and tellurium. In the same time a young and clever researcher (Stanford R. Ovshinsky) who founded his own company in USA, Energy Conversion Devices Inc. invented the first switching device based on a chalcogenide complex material. The search for new chalcogenide materials, phenomena and applications became a race, similar to the race for gold in the America of the 18-th century. Following the development of the glassy chalcogenide field, new optoelectronic materials based on halides have been discovered. Complex oxide and non-oxide glasses have been prepared and investigated in the last several decades, thus widening the groups of materials used in various optical, electronic and optoelectronic glasses.

The great advantages of the disordered materials are: simple preparation procedures, low sensitivity to impurities, low cost, and, last but not least, the possibility to produce large area films of various thickness in classical systems for deposition: systems for evaporation in vacuum, magnetron systems, flash, spin-coating systems, sol-gel systems etc.

In this paper we try to show the extent of the specific phenomena observed in chalcogenide glasses that makes these materials of large use and great perspective in electronics and optoelectronics.

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2. Phenomena in amorphous and glassy chalcogenides.

One of the main properties of the chalcogenide materials is their sensibility to the action of light and other electromagnetic radiations. Therefore, many effects discovered in chalcogenide disordered materials are based on the action of light.

The old and new phenomena could be ranged in a long row that is continuously enlarged.

The photo-darkening effect is defined as the shifts of the optical absorption edge towards longer wavelengths (lower energies), the so-called redshift. The effect appears when the chalcogenide glass (As_2S_3 , As_2Se_3 or other chalcogenide alloys) is illuminated by light of energy above the band gap of the material [1]. Many papers discussed the photodarkening phenomena in various materials, including polymers [2-6].

The photo-bleaching effect is the reverse effect of photodarkening. In order to get photo-bleaching, it is important to illuminate the sample at a temperature a little bit larger than that, which favors the photo-darkening. The photo-bleaching is defined as the shift of the optical absorption edge of a chalcogenide material towards lower wavelengths (higher energies) when the sample is heated under T_g or illuminated with light of energy below the band gap [7, 8].

The photo-plastic effect has been discovered and largely studied by Trunov and Bilanich [9-10]. They observed that inorganic glasses are typically brittle materials at ambient temperature and this is due to the relatively low hardness as compared to their flow limit. By applying in-situ stress measurement to photostructural changes in chalcogenide films based on As-S(Se), Trunov and Bilanich have found essential dynamic changes in film plasticity, i.e. a reversible photo-induced transition from brittle to ductile state. The effect was explained in terms of the viscous flow of glasses under band gap illumination.

Recently the negative photo-plastic effect giant softening was discovered by the same authors (2005) in $\text{As}_{20}\text{Se}_{80}$. In this case the photo-induced change in optical constants of the film is minimum.

The photo-induced fluidity effect is the flow of a chalcogenide glass under illumination with sub-band gap light. The effect was discovered by Hisakuni and Tanaka [11].

The elongation effect was firstly reported by Vonwiller [12]. He observed that the light influences the elongation speed in vitreous selenium fibers.

The photo-induced ductility effect was reported by Kastrissios et al. [13]. The effect is related to fiber elongation under the action of light. The name of the effect reflects the presence of the combined action of illumination and application of an external stress.

The optomechanical effect was discovered by a group led by Elliott [14]. The effect consists in the displacement of a cantilever with a chalcogenide film under the action of light. This displacement is the result of film internal stress relaxation or generation caused by increase or decrease in its plasticity (therefore is related to the photoplastic effect). Earlier B. V. Deryagin et al. [15] reported an optomechanical effect in As-S films.

The polarization-dependent photoplastic effect in $\text{As}_{50}\text{Se}_{50}$ chalcogenide glasses has been discovered by Trunov and Bilanich [16]. The authors have shown that band-gap linearly polarized light produces hardness anisotropy of the surface of the $\text{As}_{50}\text{Se}_{50}$ films. The light induced decrease or increase of the plasticity of the glass depends on the polarization state of the incident light.

The thermo-stimulated interdiffusion effect was observed in multilayer films of the type Se/ As_2S_3 by Kikineshi et al. [17]. Later the effect was observed in metal-chalcogenide composite multilayers [18].

The light-stimulated interdiffusion effect, discovered by Kikineshi [19] consists in the interdiffusion of the layers in multilayer structures based on chalcogenides (i.e. a-Se/ As_2S_3) under the influence of light. An effective intermixing of components at short nanometer-size distances is produced and a volume increase is observed.

The ion induced interdiffusion effect was recently reported by Ivan et al. [19bis]. The irradiation by ion beams determines the intermixing of the layers in nano-multilayers. This intermixing is accompanied by optical bleaching and volume expansion.

The photo-expansion effect consists in the increase of the volume of chalcogenide glasses under illumination. Sometimes a giant expansion effect is observed. In some films a photo-contraction effect is observed. The volume change during light induced diffusion in multilayers is due to the deviation from the Végard law during intermixing. The light stimulates the contraction-expansion effects, especially the giant photoexpansion in nano-multilayers. Giant deformations

(thickness changes up to 4-5 %) occurs under low-intensity laser illumination in a-Se/As₂S₃ nanolayer structures, similarly to the expansion effects observed in chalcogenide layers at high power illumination [20].

The self-organization effect in chalcogenide glasses stems from the discovery of Boolchand of the so-called intermediary phase (or Boolchand phase) [21]. This phase is intermediary between the floppy phase for lower dimensionality of the composition and rigid ones for the higher dimensionality of the network. The intermediate phase exists in a narrow compositional interval in several binary glasses (e. g. As_xSe_{1-x}, Ge_xSe_{1-x}) for $x \sim 0.20-0.22$. Experimental findings suggest that glasses in the Boolchand phase consist of networks that are optimally constrained and self-organized, those in the floppy phase are underconstrained and entropically stressed while those in the stressed rigid-phase are mechanically overconstrained and enthalpically stressed. The self-organization in chalcogenide glasses is discussed in the paper [22].

The athermal photo-induced transformation effect was discovered in AsSe molecular films by Kolobov [23]. Two mechanisms were suggested for this effect: photon-induced intra-molecular bond breaking which leads to a continuous random network or intermolecular bond-breaking resulting in an orientationally disordered molecular glass.

Photo-induced amorphisation effect [24]. The amorphisation has not a thermal origin but an electronic one. The driving force of amorphisation is the presence of a small amount of amorphous phase and of strains.

The laser-induced suppression of photocrystallization was discovered by Roy et al. [25] in amorphous selenium films. The films subjected to the action of two laser beams, whose photon energies are situated on different sizes of the optical band gap, crystallize much slowly than the case of the action of only a laser beam. A decisive role of the polarisations of the two laser beams has been demonstrated. The suppression of the crystallization rate is observed only for the polarisations of the two light sources to be parallel to each other. The crystallization suppression effect is due, probably, to the fact that, while the sub-band gap light creates nuclei with certain orientation of the optical axis, the cross band gap light breaks them, and vice-versa.

The photoinduced softening and hardening effect. The effect was observed in Ge-As-S films subjected to ultraviolet irradiation [26]. This effect could be explained by the special property of chalcogenides: they are soft semiconductors, due to the two-fold coordinated chalcogen atoms, which are susceptible to exhibit electro-atomic responses, and they behaves as a flexible electron-lattice coupling system.

The photo-amplified oxidation effect. In ambient conditions the photo-oxidation is triggered during exposure to light. The composition Ge₃₅S₆₅ is the most sensible composition to this process [27].

The photo-dissolution and photo-doping effects. The first one consists in the photo-dissolution of the metals into a chalcogenide alloy. A metal layer deposited on the surface of a chalcogenide film diffuses in the chalcogenide under the influence of a light beam. The effect was discovered in 1966 by Kostishin et al. [28]. Silver diffuses very easily. A maximum silver concentration in a chalcogenide film is 29.1 % [29]. The second one is related to the diffusion of various atoms at long distances, under the action of light.

The photo-polymerization effect. The polymerisation of the glass during exposure to light, accompanied by a red shift of the optical absorption edge, is a typically irreversible phenomenon, which was observed both in evaporated arsenic-chalcogen films [30] and simple chalcogenide films [31].

The anisotropy of the transmittance. This effect consists in the anisotropy of transmission when the chalcogenide is illuminated with linearly polarized light. Hajto and Ewen have shown [32] that As₂S₃ glass rotates the polarization plane of a polarised ray before light irradiation (therefore As₂S₃ exhibits natural optical activity) and, after irradiation, the rotation angle changes (therefore it exists photo-induced optical activity).

The photo-anisotropy effect. The effect was firstly observed by Weigert in 1920 [33]. Along the time the effect was observed in many materials: organic polymers, liquid crystals, oxides and in phase-separated systems. The photo-induced dichroism was also observed. The most interesting feature of a chalcogenide (As₂S₃) is the cycle negative-positive-negative dichroism produced when the annealed sample is photodarkened sequentially to 80 K and to 300 K [34]. The photo-induced

dichroism defined by $\Delta\alpha = [\alpha_{\parallel} - \alpha_{\perp}]$, and birefringence defined by $\Delta n = n_{\parallel} - n_{\perp}$, for example in As_2S_3 , are estimated to be 10^2 cm at $\alpha \sim 10^4 \text{ cm}^{-1}$ and 0.002 at $n \sim 2.6$, respectively.

Photo-induced girotropy effect. Lyubin and Tikhomirov have studied the phenomenon [35]. They suggested that the appearance of the photo-induced girotropy in chalcogenide glasses, i.e. the photo-induced circular birefringence, which leads to optical activity and photo-induced circular dichroism that leads to ellipticity, therefore the optical properties of chalcogenides are determined by the spatial dispersion.

The anisotropic opto-mechanical effect was discovered by Krecmer et al. [14]. The effect consists in a reversible anisotropic volume change induced by polarized light in a thin film of chalcogenide (e.g. $\text{As}_{50}\text{Se}_{50}$). Contraction occurs along the direction of the electrical field vector and expansion perpendicular to that direction.

The photoinduced scattering of light. There was observed [36] that the light of energy below the gap exhibits a strong photoinduced scattering. The effect was revealed by the change of the shape of the cross-section of the transmitted laser beam. Before the irradiation the image of the transmitted laser beam on a screen is circular, as for the initial beam. During irradiation a diffuse halo is formed along the original spot. The image is gradually eroded and finally is stabilised as a nebula covered by spots (speculae). Recently the effect of self-induced scattering of light when a laser beam interacts with the chalcogenide lenslets mounted on at the end of an optical fiber has been observed [37].

The transmittance oscillation effect. The observation of the transmittance oscillations was firstly done on GeSe_2 films deposited on on glass substrates. It was found that under the influence of the continuous focused He-Ne laser beam, the transmittance and the reflectance show periodic oscillations in time above a threshold of $\sim 1.6 \text{ kW/cm}^2$. Bistability and hysteresis were also found without placing the sample in an optical resonator. After some scientists the oscillatory behaviour may be associated with laser induced reversible micro-crystallization. Other scientists explains the phenomenon by laser heating and photo-induced structural changes in the films.

Anisotropic surface corrugation effect. Tanaka et al. [38] have discovered that linearly polarised light can produce an anisotropic surface corrugation in amorphous chalcogenide films of As-S-Ag. The corrugation resembles a mouth whisker consisting of narrow fringes, which are parallel to the electrical field of light, and streaks, which radiate from the illuminated spot to directions near perpendicular to the electrical field. Optical birefringence of about 0.01 appears with this pattern.

The photo-elastic birefringence effect. The elastically deformed glassy As_2S_3 show photo-elastic birefringence and dichroism [39]. In axially deformed samples unique properties do appear. When the uniaxial compression is released the frozen birefringence is accompanied by isotropic optical modifications, which can be relaxed by illumination or thermal annealing.

The thermo-dissolution effect. Kolobov et al. [40] have shown that. In the case of As_2S_3 , besides the photo-dissolution effects, are significant the thermo-stimulated dissolution of this glass at temperatures $> 80 \text{ }^\circ\text{C}$. There was observed the thermo-dissolution of zinc in As-S-Se, Ge-Se and Ge-S.

The switching (Ovshinsky) effect [41]. In 1959 Stanford R. Ovshinsky observed the switching phenomenon. He demonstrated in 1968 the switching effect in an amorphous chalcogenide material. The switching effect consists in a sharp transition from high resistivity to low resistivity of the material when an enough large electrical field is applied. The current controlled negative resistance is an essential phenomenon for making computer superintegrated memories. Two kinds of switches were described: threshold switches and memory (bistable) switches.

The γ – radiation induced effects: oxidation, hydrogenation, hydration, hydrocarbonization in a chalcogenide glass As_2S_3 have been discovered by Shopotyuk starting with 1987.

Deuteron-radiation induced effects were discovered by K ok enyessi in 2003. Darkening and increase of the film thickness (AsSe and As_2S_3) have been observed (S. K ok enyessi et al., J. Non-Cryst. Solids 326&327, 209 (2003)).

The polarization effect or the electret effect. The dark high field polarization was observed in As_2S_3 by Kolomiets and Lyubin in 1962 and by Andreichin in 1970. The effect does appear when the chalcogenide sample is mounted between two electrodes and is subjected to a high electrical

field. The largest amount of electrical charge is accumulated at the surface of the sample. The dark depolarization begins immediately after removing the field and fully disappears after a half-hour.

The photo-polarization effect. A polarization effect was observed when the chalcogenide glass sample is illuminated. For photopolarization in As₂S₃ minimum photon energy of 1.3 eV is needed. The photopolarization state increases considerably for higher energies. The photoelectret effect is characterized by prolonged preservation in dark of part of the photopolarization.

The acoustic-optical effect is set up when an ultrasonic wave is passed through a material, causing variations in refractive index to give an effective acoustic diffractive grating within the glass. A laser beam travelling in a plane perpendicular to the direction of travel of this acoustic wave will be deviated from its original path by an angle depending on the frequency of the acoustic grating. The amount of diffracted light depends both upon the efficiency of the glass and upon the amount of acoustic power launched into the test sample.

3. Optical, electrical and optoelectronic applications of the chalcogenide glasses

The chalcogenide glasses are typical solids for infrared applications. The transparency of these glasses depends on composition and is situated in the range 0.5 – 7 μm for sulphide glasses, in the range 0.8 – 12 μm for selenide glasses and 1.2 – 16 μm for telluride glasses. The glasses exhibit high refractive indices ($n=2.70$ for As₂Se₃ glass and 2.35 for As₂S₃ glass). They found applications in optical fibers for the transmission of infrared radiation.

Real-time holographic information storage is one of the most important applications of amorphous As₂S₃ films [42]. The recording is based on the photo-structural modification effects, a phenomenon specific only to non-crystalline chalcogenide. The diffraction efficiency exceeds 80 % and spatial resolution is 9700 lines/mm.

The photo-plastic effect was used to fabricate refractive lenslets in As₂S₃ glasses as shown in [43]. The effect of nano-scale photo-induced plasticity in chalcogenide glasses finds applications in the technology of chalcogenide films production and in devices for nanoimprint lithography and opto-mechanical data storage.

The photo-thermal recording of optical information is based on the photo and thermally induced effects in chalcogenides. The following steps are used: light absorption, material heating, melting, evaporation, and local ablation of the active layer or crystallization.

Reversible and irreversible recording of information has been achieved using various photo-structural effects discovered in amorphous chalcogenide films. For the reversible recording of the optical information it is recommended the use the photo-induced transformations as e.g.: amorphous \rightarrow crystal. The photo-crystallisation mechanism has been investigated by Chaudhari et al. [44]. The existence of metastable states in the amorphous material gives the possibility to make a repeated recording after a previous erasure of the inscribed information. The transition from an amorphous state (type I) to another amorphous state (type II) and the reverse transformation II \rightarrow I are both possible but the last transformation has lower probability.

For erasable recording a reversible phase transition in a thin layer of an alloy of InSb and Te is used. The optical constants of the material depend on the structure of the film. It is possible to switch the layer selectively between the crystalline and amorphous state by using different laser powers. The original state has a fine crystalline structure. During writing, localised areas of the material are melted with the help of a powerful (~15 mW) laser pulse of a short duration (50÷100 ns). The material then cools off so rapidly that the recrystallisation does not take place, leaving an amorphous area on the disk with a different reflectivity. For erasure, a laser pulse with a lower intensity (in order to ensure that the temperature of the layer remains just under the melting point) and slightly longer duration is used. This treatment causes the material to return to its original, thermodynamically more stable crystalline state.

Wang et al. [45] have shown that the reflectance of the Te-In-Sb films of composition Te_xIn_{0.6-x}Sb_{0.4} ($0.24 < x < 0.42$) increases by about 30 ÷ 45% after the specific and complicated phase transition. The films exhibit a large absorption coefficient at ~ 800 nm and may constitute a suitable medium for new optical disks.

The ability to modify the structure of thin films of chalcogenide alloys using light allows the construction of several types of imaging systems, most notably phase change optical memories. The benefits of phase change optical memories include performance, and, as a result of the inherent simplicity of the read and write processes, low cost. The key to achieving high speed is the design of an alloy where the crystallisation process involves diffusionless crystal growth in a system that does not phase segregate. These materials can be crystallised with laser pulses of 30 ns duration or less, and such high crystallisation speed allows the use of the recording media in the direct-overwrite mode. Ge-Sb-Te alloys show excellent characteristics for such application, including fast transition times and excellent stability [46]. Stoichiometric GeTe also shows good performance, but the addition of Sb extends the performance to a wider compositional range, improving manufacturability.

The technique, which uses the photo-crystallisation effect, is called ovography (after the name of the inventor: Stanford R. Ovshinsky). In the ovographic record the thickness of a recorded point is $\sim 1\mu\text{m}$ and this size gives a density of $5 \times 10^6 \text{ bit/cm}^2$ (for 3 mm distance in the row and 6 μm distance between the rows). The rates of $2 \times 10^8 \text{ s}^{-1}$ for the recording of information are possible when the phase transition from polycrystalline state to glass is used.

For photographs, a stable selenium glass film of thickness 100 nm on transparent substrate is used. After illumination with 10^{-4} J/cm^2 the image is seen in reflection as positive (contrast 20:1) and in transmission as negative. One light quantum transforms about 100 selenium atoms in the crystallite. The resolution is ~ 100 lines/mm. By application of tellurium based films it is possible to improve the image contrast by a careful thermal processing.

The scientists and technologists from Matsushita Electric Industrial Co. have discovered an interesting material with the composition TeO_x having very good properties of reversibility (they succeeded to operate one million of cycles recording-erasure-recording in the same film) stable properties and high photo-sensitivity [47]. The optical disks with TeO_x films were obtained by evaporation of the active material from two sources (Te and TeO_2) and deposition on PMMA and thus good heterogeneous films Te-TeO_2 were formed. The optimal compositions for optical recording are those with $x = 1.1$ and 1.2 . The TeO_x films are amorphous. The annealing of the virgin (as-prepared) films does not modify very much the structure although the stability of the film parameters is considerable improved.

The recording in the TeO_x films is based on the change of the transmission through the film. The transition temperature in TeO_x varies from 350 K for $x = 0.8$ to 400 K for $x = 1.2$. For practical purposes are used films of thickness 140 nm deposited on PMMA. The writing is carried out with $\lambda = 830 \text{ nm}$ at a pulse power of 8 mW and the inscribed point has the size of $0.8 \times 0.8 \mu\text{m}^2$. For the composition $\text{TeO}_{1.1}$ the ratio signal/noise is 59 dB and the energy necessary for writing is 1.6 nJ.

There were investigated complex compositions with reversible properties as e.g. $\text{Se}_{20}\text{In}_{35}\text{Sb}_{45}$. Amorphous films of $\sim 90 \text{ nm}$ in thickness were prepared and the recording was performed on the basis of the amorphous \rightarrow crystal transition. For writing are necessary high power and short pulses: $3 \div 10 \text{ mW}$ and $50 \div 2000 \text{ ns}$, the energy being $0.2 \div 20 \text{ nJ}$. For erasure must be used pulses of power $1 \div 5 \text{ mW}$ and pulse duration of $0.1 \div 10 \mu\text{s}$, at the energy of 50 nJ. For reading are used semiconductor lasers with the power of 0.1 mW. The information is stored at the room temperature during some months and the number of possible cycles is of $\sim 10^6$. Table 4.6 shows some usual materials for photo-thermal recording.

Reversible phase-change optical recording materials such as GeSbTe and InSbTe ternary systems have been developed and good practical performance has been reported. Ag-In-Te-Sb quaternary alloy has been studied. Iwasaki et al. [48] obtained complete erasability with the composition $\text{Ag}_{11}\text{In}_{11}\text{Te}_{23}\text{Sb}_{55}$ at linear velocity of around 7.0 m/s and Handa et al. [49] obtained good performance with the composition $\text{Ag}_{12.4}\text{In}_{3.8}\text{Te}_{28.8}\text{Sb}_{55.0}$ at the CD linear velocity. Matsushita et al. [50] studied recently similar ternary compositions for use as computer memories and erasable compact discs and found the highest number of cycles ($\sim 10^6$) for $\text{Ag}_8\text{In}_8\text{Te}_{46}\text{Sb}_{38}$ which exhibits the largest reflectivity difference ($\sim 26\%$) between the as-deposited and the annealed state at $\lambda = 830 \text{ nm}$.

The recording regime for some photo-thermal materials is given in table 1.

Table 1. Photo-thermal materials and the working regime.

Mechanism of recording	Material	Recording regime
Crystallisation	$\text{Te}_{81}\text{Ge}_{15}\text{Sb}_2\text{S}_2$	514.5 nm; 1-16 μs 100-10 mW
Amorphization	$\text{Te}_{88}\text{Ge}_7\text{As}_5$	580 nm ; 2-5 ns 0.015-0.030 J/cm ²
Evaporation	$\text{Se}_{97.5}\text{S}_{2.5}$	600 nm ; 4 μs ; 800 nJ

Nippon T&T Public Corporation developed recording media based on $\text{Ge}_{30}\text{As}_{25}\text{Se}_{45}$ and $\text{Ge}_{10}\text{As}_{40}\text{Se}_{50}$ glassy films. The recording is based on the photo-induced structural transformations in these glasses.

Although phase-change technology has long been recognized for the simple record and read processes it uses, the commercial success of erasable phase-change optical memories has been predicated on their capability to be used in a direct overwrite mode. Direct overwrite is the replacement of pre-existing recorded data with new data in a single exposure to a laser beam. Compared to currently available magneto-optical storage disks, which require one revolution to erase existing data, followed by a second revolution to record new data, information can be recorded up to twice as fast using direct, overwrite phase-change media. In order to qualify for use as a direct overwrite media, phase-change optical memory materials had to be developed, which could be crystallised using the same duration of laser exposure, which was used to make them amorphous. This requires the crystallisation process to be very rapid. Gonzales Hernandez et al. [51] have studied the transformation kinetics induced by diode laser pulses in Ge-Sb-Te films having compositions on the GeTe – Sb_2Te_3 pseudo-binary line and concluded that they exhibit adequate crystallisation speed to be used as media in optical memories. The highest crystallisation speed is achieved in materials, where the atomic configurations in the amorphous and crystalline phases are similar. Films with compositions Ge: Sb: Te / 50.5: 3.5: 46/ 50.5: 1.5: 48/ 32: 12: 51/ 24/21/55/ 14: 29: 57/ exhibit crystallisation when exposed to infrared diode laser exposures for less than 50 ns and are stable at ordinary temperatures.

The non-erasable recording is realised by irreversible changes in the recording medium. The media for irreversible recording using glassy chalcogenides can be situated in two categories:

1. Materials whose recording properties are based on chemical and physical effects. These changes can be:

- a. removal of the material (ablation)
 - b. photo- and thermo-stimulated diffusion of the metal (Ag,Cu) in the chalcogenide glass.
2. Materials for recording based on the thermo-stimulated reaction between the elements.

In the case of ablative recording the laser pulse creates holes in the active layer of a tellurium alloy. Because the mirror layer is locally removed, the reflection decreases at such points.

The laser recording based on chalcogenide medium provides stability of the optical disks both on storage and on multiple reading. The laser recording medium is designed on the principle of the thermochemical reaction between a chalcogenide glass and a metal or compound during illumination with short laser pulses.

The laser recording medium offered by Konstantinov and Starbov [52] is especially suitable for the spectral region above 700 nm. Only the metal absorbs the laser pulse but this effect leads to the melting of both substances, to their mixing and interaction. By quenching the melt one obtains a metal-chalcogenide compound. The combination metal-chalcogen must be chosen so that the final compound is transparent for the laser beam (above 700 nm). An example is the combination $\text{As}_2\text{S}_3/\text{Bi}$ that by illumination with laser pulses gives rise to As-S-Bi glass.

If the metal is dispersed into the chalcogenide matrix, then the thermal losses will decrease strongly since chalcogenides are poor heat conductors.

The experiments have shown that with the combinations $\text{As}_2\text{S}_3/\text{Te}$, $\text{As}_2\text{S}_3/\text{Bi}$ or $\text{As}_2\text{S}_3/\text{In}$ it becomes possible to reach energies for recording below 0.1 nJ/ μm^2 . It is expected that with refractory but resistant to oxygen and moisture materials (e.g. Ge) is possible to achieve energies of

recording in the normal required interval of $0.1 \div 1 \text{ nJ}/\mu\text{m}^2$ without encountering problems associated with the stability of optical disks to moisture and oxygen.

Direct electron-beam writing have been reported in amorphous Ag-Ge-S films: $\text{Ag}_x(\text{Ge}_{0.3}\text{S}_{0.7})_{1-x}$ [53]. Oldale and Elliott [54] reported the extreme sensitivity to electron-beam radiation of thin Ag-Ge-S films with low Ag content ($2 \div 28 \text{ at.}\%$ Ag), e.g. $\text{Ag}_{0.23}\text{Ge}_{0.23}\text{S}_{0.54}$. They demonstrated the feasibility of reversible electron-beam writing on a submicron scale. The writing process entails the e-beam-induced depletion of Ag in the irradiated area. The Ag displaced from irradiated region piles up in the form of a halo of Ag-enriched amorphous material around the illuminated areas. Such an accumulation is reversible: e-beam irradiation of the halo region causes Ag depletion in a normal way. The phenomenon can be understood on the basis of thermal (beam heating) and electronic effects: the thermal gradients resulting from the electron beam incident on the film cause the lateral displacement of Ag due to the different ionic mobilities in the temperature gradient. The process is rapid because of the electron-induced enhancement of the electronic conductivity (akin to photoconductivity) which is the rate-limiting quantity.

The dendrite formation in photodoped chalcogenide films was proposed for use in a variety of devices including programmable read-only memories, programmable resistance/capacitance devices and field configurable connections. The basic device consists of two metal electrodes with a layer of photodoped material sandwiched between them. When an appropriate voltage difference is applied across the electrodes, metal ions come out of the photodoped glass and form an electrodeposit between them, thereby forming a connection.

The optical anisotropy effect can be used to fabricate a novel type of memory device using the laser-illuminated spot as a digital or analogue optical memory element. Assuming an illuminated spot with a diameter of $0.8 \mu\text{m}$ and a periodicity of $1 \mu\text{m}$, a digital memory density of $\sim 25000 \text{ Mb}$ can be achieved in an active area of 66 cm^2 which is much larger than can be achieved on CD disc memory of the same area (750 Mb). Also, using the laser reorientation effect, an extra analogue memory function can be utilized at each illuminated spot. Using 2° as the minimum distinguishable step, 180 analogue steps can be utilized at each spot.

The need for imaging at the submicron scale has imposed new research in the field of the photolithography, mainly in two directions:

- a. the increase of the resolution of the exposure systems by turning away from the visible region of the spectrum to far UV, X-ray, electron and ion microlithography
- b. the development of new photoresist systems.

The problem with the photoresist is the conflicting requirements: high resolution and low defect level. High resolution imposes the use of thin resist layers ($0.1 \div 0.2 \mu\text{m}$) while low defect level (and also etch resistance) require thicker films ($0.4 \div 0.6 \mu\text{m}$). On the other hand thick resist films require the use of high image quality, good contrast and, therefore, the optics must be adequately tuned. By reducing the thickness of the photo-resistive part of the resist film down to $0.05 \mu\text{m}$ the requirement for image contrast could be lowered by a factor of $2 \div 3$. Thus, the cut-off spatial frequency increases, the defocusing tolerance increases too and it is possible to get a higher coherence factor, i.e. shorter exposure times. With existing lenses of numerical aperture $\text{NA} = 0.3$ the resolution is limited in that case by the wavelength only.

Lower image contrast allows for using lenses with low numerical aperture, therefore greater field size, the placement of multiple chips in a single field and larger chip sizes. The defocusing tolerance that is important for copying on relief surfaces is increased accordingly.

After the discovery of the effect of photo-stimulated modification of the solubility of the chalcogenide As_2S_3 various applications in technology emerged. Thus, the way was opened for producing new offset plates and a new photoresist for high-resolution microelectronics circuitry. Due to the sensitivity of the chalcogenides to electronic and X-ray beams it was possible to get special resists of very high resolution. Excepting microelectronics, the photoresists can be used successfully for making precise diffraction gratings as well as amplitude and phase zone plates in optics.

The increase of the solubility rate in ammonia with $\sim 18 \%$ by illumination was used in the photo-masking technique. A resolution of $\sim 3000 \text{ lines/mm}$ was reached. The effect can be enhanced when the chalcogenide films ($0.03 \div 3 \mu\text{m}$ thickness) are covered with thin metal films (e.g. Ag or Cu: $0.03 \div 0.05 \mu\text{m}$ thickness). The activation of the chalcogenide glass by irradiation in the range of

optical hole band through the semitransparent metal film is related to the photo-induced diffusion of metal in chalcogenide films.

The chalcogenide glasses show mostly a strong resistance against acid solutions, whereas these glasses are dissolved easily in alkaline solution.

An inorganic photo-resist was developed by utilising the sputtered Ge-Se films which can be used both for positive and negative-type photo-resist by applying the two photo-chemical effects: i) the dissolution rate into alkali solutions gets higher by illumination of the film and ii) the chalcogenide glasses become almost insoluble into alkaline solutions by the photo-doping with silver.

The As_2S_3 amorphous films exhibit the necessary properties for the preparation of imaging layers sensitive in the wavelength range $350 \div 550$ nm. The low crystallisation aptitude allows getting thin homogeneous and stable films. In the system As-S the photo-induced modifications are very strong. The optical absorption edge shifts towards red part of the optical spectrum with $\sim 4\%$, the refractive index increases by $\sim 5.4\%$, the dissolution rate increases by 40% and the photo-induced vapourisation is $\sim 10\text{-}20\%$ [55].

The luminous image obtained in As_2S_3 film is stabilised by selective dissolution in alkaline solutions of the exposed and not exposed areas. As a result, a positive or negative image appears.

Some studies have pointed out that the increased arsenic content in As_2S_3 layers causes an enhancement of the stability against alkaline solutions.

In applications are used both pure As_2S_3 films and combinations with metals as e.g. silver. The arsenic sulphide is very resistant against acids, especially fluoro-hydric acid and this property allows for preparing chromium-based masks.

The advantages of the inorganic resist over the organic one are: good uniformity on large areas and small thickness. Moreover, the technology is able to ensure the purity conditions in the fabrication of resist films in the same vacuum cycle.

Buroff [56] succeeded to reproduce the details of $0.35 \mu\text{m}$ and achieved the theoretical limit of the lens resolution. The electron micrographs reveal no traces of standing wave effect in spite of the high reflectivity of the chromium layer. Simultaneous printing of large ($5 \mu\text{m}$) and small ($0.5 \mu\text{m}$) features were demonstrated. The system developed by Buroff provides a number of technological advantages. The rate of condensation, the substrate temperature ($5 \div 40$ °C), the composition and the residual pressure in the vacuum chamber ($10^{-4} \div 10^{-5}$ Torr) do not affect the resist properties. An important factor is the evaporation temperature that can be easily controlled. The development temperature and the pH of the developer can vary in the limits 22 ± 2 °C and 11.5 ± 0.1 °C, respectively.

Printing plates of the type "offset" with positive sensitivity have been prepared in the Laboratory of Photo-processes of the Institute of Physics of the Bulgarian Academy of Sciences in Sofia, in 1980. A positive image has been obtained by selective dissolution of an As_2S_3 film evaporated on an anodised aluminium surface. The not dissolved areas are hydrophobic and therefore are sensitive to ink, while the free aluminium surface is hydrophilic and does not attract the ink. The printing is carried out with a perfect quality and the life of the plate is ~ 50000 printing cycles.

Since As_2S_3 is not resistant to dry etching, other systems were invented.

For this purpose the interaction metal-vitreous chalcogenide was proposed. A smaller thickness of the photoactive zone is achieved on the metal/semiconductor boundary ($0.02 \mu\text{m}$). The high resolution and contrast is facilitated by the concentration of the reaction products in the photoactive zone and, therefore, the diffusion of the metal only in the illuminated areas, with the result of an edge-sharpening effect. The reaction product is very resistant to plasma etching, displays an excellent protective ability and avoids the standing wave effect due to high absorption efficiency in the UV region.

Negative offset plates have been produced on the same principles, by using the combination $\text{Ag}/\text{As}_2\text{S}_3$. In this case, after irradiation, the unreacted components are selectively dissolved. The product of the photochemical interaction remains on the substrate and thus the printing element is created. For such printing system a more complicated treatment is needed and still the life of the plates, expressed in number of copies, is relatively small.

The selective dissolution of the chalcogenides gives the possibility to use these materials for getting phase objects in relief (holograms, phase filters, optical integrated units).

A special multilayer design for a photo-resist with excellent resolution and more simple processing as compared to the conventional microlithographic resist was recently developed by Kozicki et al. [57].

The modern trend towards higher integration level in the monolithic circuits is strongly related to the realisation of enhanced packing density of the electronic components on very low areas. The reduction of the size of the integrated circuit plates is essentially dependent on the advances in the lithographic technique. The gradual reduction in size of the circuitry is in close relation with the capacity of the optical systems combined with the contrast possibilities of the photoresist. Today, the optical conventional resists (organic) are inferior to the organic ones as regarding the contrast. An additional limitation of the resolution stems from the fact that the organic resists uses wet substances in the developing stage and these are unable to dissolve the material in narrow spaces. That is why it is suitable a photo-resist system with very high contrast and with the possibility to be dissolved in dry conditions.

A multilayer-planarized system of the type As/S/Ag, called PASS has been developed on non-photo-active substrate. The active film was As-S with a very thin layer of silver deposited on it by evaporation or sputtering. When exposed to light (or other radiation of energy close to the optical gap of the chalcogenide glass: 2.5 eV) silver diffuses in arsenic sulphide and forms a ternary compound with properties very different from those of the basic material. The complex layer of arsenic sulphide and silver has the thickness of ~ 200 nm, while the silver upper layer is only 40 nm thick, enough for permitting the light to pass through. As-S is stable in the CF_4 plasma and the ternary compound is highly insoluble.

When the image is developed, after the elimination of the unreacted silver by a wet procedure, then the As-S regions are eliminated by plasma etching or by reactive etching with CF_4 in order to expose the underneath planarized layer. The remained (unetched) ternary layer zones are used for selective protection of the planarized layer. Thus it is possible to develop in a dry procedure the resist. This procedure gives rise to a negative image of the applied mask. A positive image is produced if a different sequence during developing is followed: in the first stage is used sulphur plasma that dissolves the ternary compound but not the arsenic sulphide. In the second stage is performed the etching in oxygen plasma with the purpose to etch the underneath planarized layer.

The optimum material for this lithographic scheme is As_2S_4 that forms a homogeneous system of ternary glass without phase separation when is combined with the appropriate amount of silver. Because the active material has no large macromolecule components, the theoretical resolution can be reduced down to several nanometers. Other chalcogenides, as for example the germanium selenides exhibit a larger lateral diffusion and, therefore, the metallic elements will diffuse (thermally) in the absence of the light. It results therefore, that the system As-S/Ag seems to be an ideal system for lithography. As_2S_4 can be deposited easily by evaporation and its stoichiometry can be controlled without difficulty.

In order to reach the optimum concentration of Ag in As-S, the thickness of the As-S layer must be situated after photo doping at a value corresponding to $3 \div 5$ times the thickness of the Ag layer. This results in the formation of a ternary alloy situated in the middle of the glass formation domain as shown in the ternary phase diagram.

The PASS scheme is very sensitive to the electron beam and, therefore, it is possible to inscribe details below 100 nm for line dose 5×10^{-10} C/cm. The Ag layer above the chalcogenide one plays an important role in the diminishing of the electrical charging of the layer during electron beam exposure. The PASS method succeeded to eliminate most part of the disadvantages of the conventional photo-resist, including also the problems of the focusing depth.

Many multilayer configurations have been tried.

In the photo-passive polymer bilayer scheme, a Ge-Se layer is evaporated on a polymer planarizing layer or a photoresist-planarizing layer is used. In both cases a silver layer is deposited onto Ge-Se from one of the following solutions of silver ions and complexes: $AgNO_3$, $KAg(CN)_2$, $Ag(SCN)_4^{3-}$, Ag(alanine), $Ag(NH_3)^{2+}$, $Ag(CN)_2$. After image-wise exposure unreacted silver and Ge-Se are removed. The remaining reaction product protects the sublayer during dry etching. With the photoactive system etching of the resist could be carried out (with a developer) after the uniform

illumination of the sample (the reaction product serves as a mask). The system AgSe/Ge₂₅Se₇₅ has the additional advantage of the anisotropic etching of Ge₂₅Se₇₅ that possesses a columnar structure and dissolves vertically without undercutting. Thus, the three-component system: planarizing polymer layer - Ge₂₅Se₇₅ - thin photoresist layer, combines high sensitivity and resolution without undercutting and standing wave effects. GeSe₂ serve as an insulating layer between the photoresist and the planarizing sublayer as well as a reliable protection upon plasma etching.

The basic disadvantage of these systems is the deposition of silver from solution prior to exposure. This is necessary since the thin metal layer is not stable when in contact with the atmosphere and diffuses in the volume of the semiconductor in some tens of hours. Furthermore, the deposition process itself is quite irreproducible and imposes measurements of each batch of samples.

The reverse system where the silver layer is deposited between the substrate and the photosensitive layer is more appropriate and more reproducible. In that case, too, the reaction products accomplish their protective function.

Another possible solution to the problem is the deposition of the metal in the form of some chemical compound AgCl, Ag₂S, AgI. The use of AgCl leads to an increase in the reactivity but the resolution drops due to the formation of clusters with sizes up to 150 nm. During electron beam exposure AgCl decomposes but Ag does not migrate in As₂S₃ so that an intermediate UV exposure is necessary (sensitivity of 85 $\mu\text{C}/\text{cm}^2$ is achieved).

The combination AgBr/As₂S₃ provides a possibility for considerable increase of the sensitivity; it rises by nearly two orders of magnitude. After exposure the bromide layer is developed. Upon subsequent illumination the developed silver reacts with As₂S₃. The system could be appropriate for use with expensive exposure devices as e.g. X-ray or e-beam units.

The addition of a third component from the third group of the periodic table to the Ge-Se system provides new opportunities for the photoresist technique. Films of composition Ge-Se-A^{III} where A^{III} is Ga, In or Tl have been studied. Films with 5, 10, 15 at.% metals and 5 and 10 at.% Ge were prepared. The film starts to transmit above 500 nm wavelength.

In the kinetic dissolution curves a negative effect of photo-stimulated dissolution was observed. The non-irradiated films exhibit a relative good resistance against etching, the ratio between the times for complete dissolution of the irradiated and non-irradiated areas being around 5.

The unusual contraction effect induced by UV radiation in Ge-As-S thick films suggest the application of these materials for photo-plastic recordings of images (printing plates) without the need of selective etching procedures.

The sensitivity for visible and X-ray radiation makes the chalcogenide materials very promising for high-resolution photo-resist, even in the lithography. For X-ray imaging are used plates of amorphous selenium on aluminium substrate. Selenium is doped by 0.2 ÷ 0.5 at.% As and by small amounts of chlorine. In the electroradiography the electrostatic image results by the exposure to X-rays of the object and the image is read by using scanning techniques. Finally, the image is converted in a digital form for storage and computing. Ultrahigh resolution photolithography was demonstrated using Ag-Se/Ge-Se resist and X-ray synchrotron radiation.

The modern electron beam lithography enables the realisation of increasingly sophisticated diffractive optical elements, which are based on the diffraction of light by microstructured surfaces. Ideals resist exhibits high resolution and sensitivity, linear dependence of profile depth on electron dose, and good profile-shape repeatability. The resist should be suitable for the preparation of nickel shim masters, which are used in the low-cost replication processes of diffractive optical elements.

The photoelectric properties of the chalcogenides (photoconductivity, photopolarization, and photoelectret state) have been utilised in the development of several methods for measuring the radiation.

Among the vitreous materials with applicability in radiometry are pure As₂S₃ or As₂S₃ doped by metals (Sn, Ge, Cu, Ag...), arsenic sulpho-selenides (As₂(Se_{1-x}S_x)₃), complex compositions (As₂S₃·As₂O₃), etc.

The applications in the memory radiometry are based on the remarkable photo-polarization properties of the chalcogenides, i.e. accumulation of electric charges under the simultaneous action of the light and of the electric field, the storage of the polarisation in darkness and its destroying (by flowing an electrical current in the circuit) in the absence of the external electric field when the sample is illuminated.

The change in time of the local electrical resistance of the transmission coefficient, of the reflection coefficient and of the physical parameters of the thin film structure Al-Chalcogen-Conductor during the application of an electric field allows to use solid state integrator of the quantity of electricity in systems for the control and measurement of the working time of various equipments or installations, in automation and computing technique.

The integrator allows getting an output parameter proportional to the integral of the action in time of an external parameter with very low power consumption. The reading of the information is carried out without erasure.

The solid-state integrator based on chalcogenide materials consists of a conducting and transparent basis, e.g. SnO₂, a thin film of chalcogenide glass with variable thickness and a counter-electrode from aluminium. A source is introduced in the circuit.

The mode of operation is the following:

The power source is connected to the integrator so as the measuring electrode has positive potential. In this case the electrical field stimulates the chemical transformation of the aluminium counter-electrode in the layer of the transparent dielectric. The transformation rate is determined by the value of the current flowing through the structure, that depends on the properties of the active layer and on the electrical field.

The non-uniform thickness of the active layer ensures a non-uniform distribution of the intensity of the electric field along the measuring counter-electrode and the non-uniform transformation of the last one. If the active layer has the shape of a wedge, the amount of electricity is determined visually after the magnitude of the shift of the colour boundary observed on the metal measuring electrode.

The estimation of the quantity of electricity that goes through the integrator can be realised by measuring the electrical resistivity, the optical transmission, and the integrator reflection as a whole or as separated elements.

The necessary current for the integrator is small and depends on the chalcogenide composition, on its thickness, on the area of the measuring counter-electrode, on the value of the applied voltage and has the order of magnitude of $10^{-6} \div 10^{-8}$ A. The electrical resistivity of the integrator changes in time when a constant voltage is applied: $V = 3V$. During long-time field application ($t \sim 5 \times 10^3$ h) the electric resistivity of the integrator rises with about three orders of magnitude.

The acousto-optic effect provides a method of optical signal manipulation without using high voltages. Its use in the far-IR ($6 \div 12 \mu\text{m}$) has been previously limited by the low efficiency of the commercially available materials, but the benefits from acoustically controlled frequency modulators and beam splitters make viable research into new, more efficient acousto-optic materials for mid and far - IR.

The efficiency of an acousto-optic material is characterised by its figure of merit, M :

$$M = n^6 p^2 / \rho v^3 \quad (1)$$

where n is the refractive index, v is the sound velocity, p is the photoelastic constant and ρ is the density.

The greatest effect on M is given by n .

A good material must exhibit: a) high optical transmission in the required wavelength range b) stability under normal application conditions ($T < 100$ °C) and c) low acoustic attenuation. The material must be fabricated to a high degree of uniformity and enough large size for commercial devices ($1 \text{ cm} \times 1 \text{ cm} \times 5 \text{ cm}$).

Acousto-optical devices can rapidly modulate the amplitude and direction of a laser beam. An rf field is applied to a block of suitable material and an acoustic grating is thus generated within the block. The grating can be used to produce two optical beams and the measurements of the particle flow are then possible at the point of recombination of the beams. Far IR chalcogenide glasses, when suitable formulated to optimise the acousto-optical figure of merit, are attractive for operation at $10.6 \mu\text{m}$.

The heating effect produced by incident rf power means that application of the glass in acousto-optic devices may be limited by thermal expansion mismatch between components at elevated temperatures and by glass stability.

The system As-Se-Te was mainly studied due to its higher stability and diminished phase separation aptitude. Sb, Ge and Pb have been used as dopants (5 ÷ 10 at.%) .

For shorter optical wavelength operation there were investigated glasses in the system Ga-La-S. Glasses in the chalcogenide system based on $\text{Ga}_2\text{S}_3 - \text{La}_2\text{S}_3$ has been found to exhibit relatively high acousto-optic *figures of merit*, low acousto-optic losses and high acoustic velocity. These properties combined with the transparency both in visible and infrared (0.5 ÷ 10 μm), high refractive index, non-toxicity, high softening temperatures (e.g. $T_g = 561^\circ\text{C}$), enough high damage threshold, ease of fabrication, optical quality, chemical stability and isotropic properties make it attractive for acousto-optic device applications. The interest in this glass system was awakened in the last years due to its low phonon energy, hence acting as a promising host for rare earth elements for the development of an efficient optical fibre amplifier operating in the near infrared region. The glass can therefore be suitable for building efficient in-fibre acousto-optic devices.

The As-Se-Te-(Ge-Pb) system transmits over a wide range covering three laser wavelengths at 1.55 μm , 2.06 μm and 10.6 μm . The transmission levels are near the theoretical maximum. The reported figure of merit relative to silica, 842 ÷ 1335, seems to be very large although the results are characterised by large error bars.

The amorphous As_2S_3 is transparent in near infrared and exhibits a high figure of merit: $654 \times 10^{-15} \text{ s}^3/\text{kg}$. Addition of germanium to As-Se system increases the connectivity of the network, hence raising both TG and acoustic velocity. Refractive index is lowered and M values at 1.15 μm wavelength fall from $1200 \times 10^{-15} \text{ s}^3/\text{kg}$ for AsSe_4 to $330 \times 10^{-15} \text{ s}^3/\text{kg}$ for $\text{As}_{20}\text{Ge}_{30}\text{Se}_{50}$ glasses. The base glass As-Se-Te with 5 mole % Ge, 10 mole % Pb and $n = 3.205$, shows an outstanding figure of merit : $1880 \times 10^{-15} \text{ s}^3/\text{kg}$ at 10.6 μm . The base glass As-Ge-Se ($n_{10.6} = 2.878$) with additions of 20 mole % Te and 5 mole % Pb gave : $M = 1457 \times 10^{-15} \text{ s}^3/\text{kg}$ at the wavelength 10.6 μm .

As-S and As-Se films photodoped with Ag or Cu have been investigated as ion-selective membranes for sensing Ag or Cu ions. These films are intended for use as the membranes in ion-selective field-effect transistors. The role of the dopants is to improve the electro-conductivity of the membranes. Chemical sensors have a wide variety of uses, for example in medical diagnosis, pollution monitoring, and chemical process control.

Chemical remote sensors have been developed on the basis of chalcogenide glasses. The wide IR windows and the high resolution of Fourier transform infrared spectrometry together, permit remote sensing of several gases or liquids using their absorption due to the fundamental absorption modes, for instance by means of fibre optic-evanescent field spectroscopy. The unclad GeSeTe fibre was used to this purpose. It was possible to measure the existence of small amounts of organic and acid species in aqueous solutions quantitatively.

A new approach for the qualitative and quantitative analysis of gas species such as CO (4 ÷ 7 μm), CO_2 (2 ÷ 4 μm) and H_2O (4 ÷ 6 μm) in the coal combustion furnace. The emission spectrum of the furnace was delivered through the fibre cable to the FTIR spectrometer. The in-situ quantitative measurement of CO gas as low as 100 ppm was carried out at 1550°C .

The unstable gas CO was also successfully detected at 8.2 μm during the reduction of SiO_2 by graphite. Chalcogenide glass fibres (sulphides) were used instead of KRS-5 fibres due to higher flexibility and thermal stability of these fibres with length of more than 10 m required for the applications in the pilot plant combustion furnace.

Several chalcogenide glasses have been used as thermistors in the regulation devices for the nuclear reactors due to high neutron fluency ($\sim 10^{20} \text{ n/cm}^2$). There was studied several compositions for thermo-switches based on Te in planar thin film devices: $\text{Si}_{35}\text{As}_{30}\text{Te}_{35}$, $\text{Ge}_{18}\text{As}_{42}\text{Te}_{40}$, $\text{Si}_{37}\text{As}_{30}\text{Te}_{33}$, $\text{Si}_{12}\text{As}_{24}\text{Te}_{64}$. The best thermo-stability has been observed for the switches based on $\text{Si}_{37}\text{As}_{30}\text{Te}_{33}$. This material allows for switching in the conducting state at $\sim 200^\circ\text{C}$ without change of the current parameter up to 10 mA for 10^4 cycles. The presence of an exponential dependence of conductivity versus temperature allows using several chalcogenide glasses for making good quality thermistors.

The progress in the study of the optical fibres offers new opportunities for the elaboration of new family of devices for the measurements of the physical parameters. New sensors and

transducers of high performance have been produced on the basis of some properties of the fibres, which make possible the modulation of the transmission parameters by the physical parameter to be measured.

Big companies are interested in the research and production of sensors based on optical fibres in general and chalcogenide fibres in particular. At the end of this millennium the total volume of production for sensors based on optical fibres is estimated to 4.88 billions of dollars (Proceedings SPIE, Fiber Optic Sensors, Vol. 586, p. 2-13, 1985). A fraction of 84 % is used in military technique and 14 % in industry and medicine. The most important companies involved in this field are: AEG Telefunken, Allied Bendix, Boeing, Hitachi Ltd, IBM, Martin Marieta. 70 % of optical fibres production is by North America, 15 % is by Europe and 12 % is by Japan. There are two categories of sensors: sensors, which use the fibre as sensing element and sensors which use the fibre as transmitting medium from the object to the device.

The parameter to be measured is transformed in some optical signal following the interaction of the optical guide with the source. The high sensibility of the transducers based on optical fibres is due to high optical distance wherein the interaction with the source is realised. The working principle of the optical fibre sensors is based on the recording of several parameters of the light transmission in fibres:

- light propagation time (interferometric sensors /phase or frequency modulation/)
- intensity of the transmitted light (amplitude modulation sensors)

The sensors have the advantages of the non-sensitivity to electromagnetic fields. Moreover, they do not induce electromagnetic noise in other electronic systems. The transmission of the information can be realised at large distances and the sensors have low dimensions and low prices.

The properties of vitreous ionic conductors are of fundamental and practical interest. Glasses are suitable for a wide range of electrical and electrochemical applications. In addition there is a renewed interest in understanding the mechanisms of the ionic conductivity. Chalcohalide glasses are of prime interest. Ag^+ ion - containing chalco-halide glasses are particularly interesting because they possess high conductivity that can reach $10^{-2} \Omega^{-1}\text{cm}^{-1}$ at room temperature. In the $\text{Sb}_2\text{S}_3\text{-Ag}_2\text{S}_3\text{-AgI}$ ternary system the best conductivity obtained is $0.06 \Omega^{-1}\text{cm}^{-1}$ for molar composition $3\text{Sb}_2\text{S}_3\text{-57Ag}_2\text{S-40AgI}$ with an activation energy around 0.15 eV. There was proposed the application of chalcohalide glass in solid-state batteries.

The thio-iodide glasses show high conductivity, are very stable versus moisture and can be shaped easily as bulk material or thin film. Therefore they are good candidates for electrochemical applications. The behaviour of a silver thioiodate - silver phosphate glass was studied in a test solid state battery. A galvanic chain $\text{Ag/Ag}_3\text{SI-AgPO}_3/\text{I}_2 + \text{phenothiazine}$ was developed. The performances were comparable to that obtained with RbAg_4I_5 (a solid electrolyte) with the highest Ag^+ ion conductivity at room temperature leading to batteries capable of considerable discharge.

Various silver thioiodate glasses based on Ag_3SI have been discovered. They possess a very high Ag^+ mobility and solid-state batteries have been developed using these materials as electrolyte.

The amorphous MoS_3 has been investigated with the purpose to use it as a high-energy cathode material in ambient temperature alkali metal cells. Amorphous MoS_3 , prepared by chemical or thermal decomposition of ammonium thiomolybdate, has been found to react readily with n butyl lithium and sodium and potassium naphthalides to give compositions M_xMoS_3 ($0 \leq x \leq 4$, $\text{M}=\text{Li, Na, K}$). The MoS_3 cathodes used in lithium electrical batteries (cells) react with up to 3.8 Li per MoS_3 under constant current conditions (0.5 mA/cm^2) above 1.40 V. The mean discharge voltage of Li/MoS_3 is close to 2.0 volts which, together with high coulomb capacity results in a cell with high theoretical energy density of 1,040 Wh/g. This energy density is significantly higher than the values reported for crystalline transition metal \rightarrow sulphides. Li-MoS_3 cells show good reversibility for several cycles.

Over the past decades chalcogenide glasses have been studied in order to assess their suitability as passive bulk optical component materials for IR applications. The applications are closely related to the transmission of the ion radiation in ambient atmosphere.

Fortunately, the main atmosphere components, nitrogen (N_2) and oxygen (O_2) are homopolar molecules and possess neither a permanent nor an induced dipole moment, and hence do not exhibit infrared active molecular vibrations, which would result in the absorption of IR radiation. In the initial region of their spectrum from $0.75 \mu\text{m}$ to $2.5 \mu\text{m}$ (near infrared), another from $3.0 \mu\text{m}$

to 5.0 μm (middle infrared), and a third from 7.5 μm to 14.0 μm (far infrared). From the black body emittance curves it results that in order to detect relatively hot objects ($\sim 400^\circ\text{C}$) the 3.0 \div 5.0 μm window is most suitable and to detect objects at room temperature the 7.5 \div 14.0 μm window is most suitable.

There is a major interest in thermal surveillance systems at present and these practical uses of IR are concerned with wavelengths up to about 12.0 μm . In order to focus this IR radiation onto detecting systems, windows, lenses and telescopes are required made from materials exhibiting adequate transmission in this wavelength region. For low power surveillance or thermal imaging applications where chalcogenide glasses will be useful, materials are required in sizes of up to 150 mm diameter and up to 20 mm thickness.

Materials with infrared transparency in the wavelength range 8 \div 12 μm are selenide and telluride glasses. The arsenic sulphide and also the chalcogenide glasses with silicon are transparent up to ~ 10 μm wavelength. Ge-As-Se glasses (big pieces of 5 \div 13 kg) have been produced in Russia under trademark IKS-29. Technical glasses of composition $\text{Ge}_{33}\text{As}_{12}\text{Se}_{35}$ (trademark Ti20) and $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ (trademark Ti 1173) under the form of discs of diameter 70 mm and platelets of area 30×60 cm^2 have been obtained.

The applications of these glasses are: energy management, thermography, temperature monitoring, electronic circuit detection, laser technique and IR-spectroscopy as well as high-resolution optics in night image technique. As an example of the latter, the blackbody radiation emitted by room temperature objects such as the human body is situated in the range 8 \div 12 μm , where selenide – telluride – based glasses are applicable for thermal imaging.

As opposite to alkali-halogenides and alkaline-earth fluorides, the great majority of chalcogenide glasses are very stable in normal atmosphere.

Windows for recipients used in infrared spectroscopy study of acid solutions are preferably made of chalcogenide glasses.

Other optical applications are based on the high refractive index of the chalcogenide glasses. They exploit the increase of the transmission of coatings with decreased reflection. The chalcogenide glasses are used as antireflection coatings for IR filters. Depending on the composition, one can change continuously the refractive index “ n ” of these glasses from the values situated around 2 for non-stoichiometric arsenic sulphide with large excess of sulphur up to $n = 3.5$ for systems with tellurium.

The mechanical strength and the thermal stability of the chalcogenide glasses are significantly lower than those of the oxide glasses. The thermal expansion coefficient, the temperature coefficient of the refractive index and the elastic-optical constants are higher than those of the oxide glasses. Because of the comparatively small mechanical strength and chemical softness of these materials, care has to be taken to avoid damage. $\text{La}_2\text{S}_3\text{-Ga}_2\text{S}_3$ and $\text{CaS-La}_2\text{S}_3$, e.g. $(\text{CaS})_{45}(\text{La}_2\text{S}_3)_{55}$ have been proposed as new materials with improved mechanical properties and good infrared transmittance in the wavelength range 2.5 \div 16 μm , appropriate for window glasses.

Finally, we must mention the use of photo-induced anisotropy effect in $\alpha\text{-As}_2\text{S}_3$ films to realise non-linear image processing like image addition and subtraction. The same effect was applied to expose Damman gratings for multispot array generation.

The development of the integrated optics is basically related to the creation of the light conductive lines for transmitting optical information. This was possible due to the appearance of laser sources of light and light conductors with low losses. The optical micro-technologies, including new techniques and materials for micro-switches, micro-lenses, etc. are mainly directed toward the infrared optics where the chalcogenide materials started to play a leading role.

Optical fibres are important as conducting elements in the optical integrated circuits or devices. Optical materials useful for IR fibres generally need to possess the following optical properties: low material dispersion, λ^4 -dependent Rayleigh scattering, high energy band gap and long wavelength multiphonon edge.

There is a wide need for infrared fibres operating in the middle infrared regions ($\lambda = 2 \div 12$ μm) with potential applications in transmission of YAG: Er, CO and CO_2 laser energy as well as in the detection of thermal radiation emitted by warm bodies, and thermal imaging.

Through the 1980s, attention was focused on the fabrication of ultra-low loss IR fibres for telecommunication signal transmission to compete with silica optical fibres.

The first report on the electrophysical and optical properties of the optical fibres with the composition As_2S_3 , As_2Se_3 , As_2Te_3 , Sb_2S_3 , Sb_2Se_3 was published by Abashkin et al. [58]. Very promising results were achieved with ternary glasses as e.g. Ge-As-Se and Ge-Se-Te. Glasses of composition Ge-Se as well as Ge-Sb-Se ternary chalcogenides are transparent in the $8 \div 12 \mu\text{m}$ range and have good thermal, mechanical and chemical properties.

Fibres of glassy arsenic chalcogenides with the diameter of $20 \div 50 \mu\text{m}$ embedded in protective coating and without coating were produced by pulling from the glass heated up to the softening temperature or from the melt as in the case of Sb_2S_3 and Sb_2Se_3 . Considering the low mechanical strength of the fibre it results that a buffer material must protect the fibre. The most usual method is cladding with Teflon (perfluorinated ethylene propylene). It was proposed a preparation method for a fibre with glass cladding using a silica crucible. By this method was possible to draw a telluride glass which is less stable against crystallisation but transparent above $13 \mu\text{m}$. The sulphide and selenide glasses draw into unclad fibre confirmed that a loss less than 0.1 dB/m could be attained.

The measurement of the spectral transmission of the As_2S_3 fibres has shown that for the wavelengths larger than $1 \mu\text{m}$ the light damping coefficient is less than 0.5 dB/cm . The theoretical minimum losses of mid-IR chalcogenide fibres are probably limited to $>10 \text{ dB/km}$.

Development and application of chalcogenide optical fibres with high performance features has been impeded by two factors: insufficient degree of purity of the glasses and their tendency towards crystallisation.

Excepting the optical fibres the thin films waveguides are fundamental media for the integrated optics. On their basis is studied the construction of the devices for introducing, processing and extraction of the information and its transmission at various distances.

The thin film planar waveguides consist of dielectric layers whose refractive index is higher than that of the substrate and of the other layer. This ensures the use of the total reflection phenomenon for directing light without losses. In the same time we must have low losses ($\sim 1 \text{ dB/cm}$). Losses as low as 0.4 dB/cm were obtained for the case of $\text{As}_{40}\text{Se}_{10}\text{S}_{40}\text{Ge}_{10}$ amorphous composition. High optical transparency of both film and substrate and the absence of light scattering must be ensured for a good waveguide.

The most interesting wavelength range for laser communication lines is VIS, near IR and the radiation of $10.6 \mu\text{m}$ of the CO_2 laser used for processing and transmission of signals of the laser locators.

For laser transmission lines the chalcogenide glasses are very promising because these materials show high transparency in infrared, high values of the refractive index ($n \sim 2.0 \div 3.4$) and can be easily obtained as wires or thin films. Moreover, it is possible to achieve matching with other waveguides like Al-Ga-As or LiNbO_3 in hybrid structure.

In the applications as thin films waveguides the chalcogenide glasses proved to be different from the other materials because they allow for recording the optical information and, in particular, the phase holograms for unlimited resolution (10^4 lines/mm) and high diffraction efficiency ($>80 \%$).

Thin film optical waveguides have been prepared using amorphous As_2S_3 layers. The layers have been evaporated in vacuum on glass substrates ($n = 1.51$), crystalline quartz ($n = 1.54$) or lithium niobate ($n \sim 2.2$). The measurements show that the minimum losses for light in the thin film waveguide is $\sim 3 \text{ dB/cm}$ for $n = 2.470$ and 2.462 for $\lambda = 0.63$ and $1.15 \mu\text{m}$, respectively. These values show that although the losses are not very low the As_2S_3 can be used for thin planar optical waveguides.

The change of the optical parameters of the chalcogenide films under the action of light (in particular the change of n) allows to produce special waveguides shaped as narrow parallel bands. They are prepared with a contact mask ($20 \div 60 \mu\text{m}$) illuminated by a He-Ne laser ($\lambda = 0.4416 \mu\text{m}$, $p > 20 \text{ mW/m}^2$).

The surface scattering has a considerable contribution in a monolayer waveguide due to surface irregularity. In multilayered As-S structure (e.g. $\text{As}_2\text{S}_5\text{-As}_2\text{S}_3\text{-As}_2\text{S}_5$), the influence of surface roughness is diminished. High performance planar wave-guides with attenuation less than 0.5 dB/cm were obtained, by realising a structure of variable refracting index using the same chemical composition and changing only the evaporation temperature.

The change of the refractive index in chalcogenide films under the action of the radiation was used for producing optical elements with thin film phase and elements of integrated optics (kinoform elements).

In order to record kinoform optical elements the films of As_2S_3 with the thickness $6\div 8\ \mu\text{m}$ were used. Such a thickness is optimum for a phase shift up to 2π in the irradiated regions when the recording is performed by an Argon laser and the reading by a He-Ne laser.

In order to produce saw-like change of the refractive index in the chalcogenide films the procedure of successive scanning over the film with a light spot in triangular shape has been used. The Argon laser beam was directed to a mask with triangular cut in it. By successive recording such triangular profiles of width $50\ \mu\text{m}$, a kinoform prism was obtained.

Kinoform cylindrical lenses have been recorded in chalcogenides. A more complicated mask consisting of twelve different triangles was used. An array of kinoform cylindrical lenses has been recorded. With this technique it was possible to reproduce kinoform optical elements in quantity, to make complicated spatial phase filters, aspherical lenses and other optical elements which are produced by mechanical treatment of glass with difficulty.

By means of the contact exposure it has been made also phase gratings, Fresnel zone plates, random phase masks, a phase filter performing Hilbert transform.

The chalcogenide materials allow getting important optical processors. It was possible to produce waveguide lenses, geodesic lenses and Lundberg lenses.

The geodesic lens is a non-planar part of the waveguide with the shape of a cupola. Lundberg lens is a three-dimensional lens where the refractive index increases smoothly from the index value of the waveguide border to a maximum value in the centre of the lens. The creation of these lenses is a difficult task. The advantage of the chalcogenide glasses is the possibility to use the laser for the local modification of the optical parameters. The Lundberg lenses were obtained by deposition through a diaphragm of variable radius. The correction of the lens needed in this case is carried out by exposing the border part of the lens to a laser radiation.

By making use of the photo-induced phenomena in chalcogenide glasses it should be possible to produce diffractive optical elements for use at IR wavelengths. These elements have a potentially large range of applications in the waveband (e.g. simple gratings, mirrors, lenses and beam combiners) and may have advantages over conventional IR refractive elements as regards weight, cost and ease of fabrication.

Many chalcogenides exhibit a metal-photo-dissolution effect known as photo doping in which illumination causes metal atoms to dissolve into the glass. Both surface relief and phase gratings have been fabricated using the photo-dissolution of Ag in As-S films and diffraction efficiencies of up to 35 % at 632.8 nm and $1.5\ \mu\text{m}$ have been measured.

The glassy chalcogenide films are promising materials for passive elements of integrated optics. Light waveguides, prisms, lenses, etc. can be produced with and within thin chalcogenide films using a laser or an electron beam.

The holography can be used in the fabrication of optical elements such as grids, Fresnel lenses, etc., with high transmission in IR range, very low level of stray light (10^{-6}) and diffraction efficiency as high as 85 %. The possibility to make microlenses was demonstrated. The chalcogenide glasses can be shaped under light illumination. The fluidity of the glass is increased by illumination and, under external tension, the shape of the material can be changed. The mechanism of this increased fluidity is athermal.

Microlens arrays consist of an array of microscopic-sized lenses fabricated on a planar substrate and find applications in integrated optics, image processing and optical computing.

Microlens arrays can be found also in an increasing number of optoelectronic applications, such as optical communication, CCD cameras, faxes, and IR technology. They were fabricated by a variety of techniques, including distributed index planar techniques, resin thermal reflow and laser beam ablation. In the last years there was proposed a process, which consists in the direct one-step formation of a three-dimensional microlens array using the dependence of the etching rate on the illumination intensity typical of chalcogenide photoresist. In spite of many advantages of the method, the microlens arrays exhibited some drawbacks. The maximum sag was limited to $1.3\ \mu\text{m}$ when gray scale or continuous tone lithography with classical UV exposure sources is used. In order to overcome these drawbacks Eisenberg et al. used the thermal reflow method that avoids exposure

problems and lead to improvement of the shape of the lenses. Using a binary mask containing holes or slits, island of 3D binary shape can be formed that can be then transformed to 3D plane-convex microlenses. This is done by heating the material close to the melting point, causing reflow and formation of the desired 3D shape. AsSe_{0.1} chalcogenide films proved to be a suitable material for fabrication of the microlens arrays. The maximum sag limit caused by photodarkening effect is thus partly eliminated.

In some As₂S₃ arrays a layer of Ag was evaporated onto them and the system was exposed to UV. By photodoping Ag in As₂S₃ lens, it was possible to increase the refractive index (from 2.5 to 2.9) and hence alter the focal length of the microlenses (from 34 μm to 27 μm).

The main feature of an optical integrated circuit is the planarity of all functional elements that gives compactness and small volume to the devices that must be produced on a single substrate in a single technological cycle.

The materials able to be used in optical integrated circuits must fill the following requirements:

- a. low optical losses in the spectral range of interest.
- b. broad range of compositions in order to offer the possibility to select materials with convenient refractive index
- c. the aptitude to be deposited on various substrates without additional optical losses.
- d. the aptitude to change the refractive index and the optical losses by external factors.
- e. particular properties allowing to combine the circuit with the radiation sources and photo-receivers
- f. high fiability and stability of the elements

Many materials have been already tried, as e.g. Ta₂O₅, LiTaO₃, LiNbO₃, SiON, epitaxial layers of ZnO, ZnS, ZnSe, Cds, CdSe, GaP, GaAs, GaAlAs, InAs, films of melted quartz, epoxy resin, etc.

The chalcogenide glasses satisfy the major part of the above requirements. The glasses exhibit high transparency in IR. Thus, the As-S planar waveguide shows optical losses of < 1dB/cm for $\lambda = 1.15 \mu\text{m}$. The refractive indices of the chalcogenides are high. The chalcogenide glasses are lacking inhomogeneity that are characteristic to polycrystalline films, and are responsible for the spatial optical fluctuations. The acousto-optical quality factor is high and the materials are therefore efficient for acousto-optical modulation and for scanning of the laser radiation in a broad spectral range.

With the chalcogenide glasses it is possible to get thin planar waveguides with refractive index anisotropy. For example, the measurement of the TE and TM modes on the $\lambda = 0.63 \mu\text{m}$ in As₂S₃ optical guides gave an anisotropy of the refractive index, ($n_{\parallel} - n_{\perp}$) of 10^{-2} . The anisotropy can be controlled by additional illumination that induces photo-structural transformations in the material. The chalcogenide glasses are strongly influenced by various external factors (optical radiation, electron, neutron and X-ray beams). These particular properties allow for creating special band waveguides, grating structures and other passive or active elements.

On the basis of the dynamical changes of the intensity at the output of the thin optical waveguide, induced by the action of the radiation in the vicinity of the fundamental absorption edge of the material, an optical switching element has been developed. With yellow radiation n increases. With IR radiation n decreases. Therefore, with $h\nu > E_g$ and $h\nu < E_g$ the transmission in the optical wave guide can be controlled. The mechanism of the dynamical change can be explained qualitatively in terms of the kinetics of photo-excited carriers accompanied by lattice distortion or defect creation. In this devices, the propagation of a light beam in optical waveguides constructed with amorphous As-S films is controlled with blue (and red) light illumination that is able to modify the refractive index of the films. The devices operate as single-throw or double-throw photo-optical switches, having switching times ranging between 20 ms and 2 s. The switching time decreases considerably if the yellow radiation intensity increases and the IR radiation has low intensity. The switch-off time depends only on the intensity of the red light and decreases if the intensity increases. Nevertheless, the decrease of the intensity up to 1 W leads to the heating of the film. That is why the minimum switching time to be reached in this switching element is believed to be no less than 1 ms.

In order to improve the switching time it is necessary to operate in the pulsed regime of irradiation. Today the interaction of powerful short pulses of radiation with the optical planar waveguides based on chalcogenide glasses is one of the main preoccupations in the field of technological investigations.

Among the elements for the integrated optics of interest for future developments are: the mono and multilayer planar waveguides, the channel-type planar guide, piezo and acoustic transducers and spatial modulator for the acousto-optical waves, active optical elements based on non-linear effects appeared during the interaction of the light in planar guide.

Detailed research has been done on the electrophotographic applications of Se/Se-Te and Se/CdSe multilayers. These multilayers exhibit several properties, which make them appropriate for including in photoreceptors:

- a. the dark conductivity in a direction perpendicular to the layer planes is lower than the conductivity of the constituent material,
- b. the stability against thermal and light treatment is good and increases with decreasing sublayer thickness, and
- c. the spectral response of the selenium-based photoreceptors can be shift towards the red part of spectrum in order to be used in the same diode laser printer, without decreasing their stability.

Most modern photocopying machines employ a-Se_{1-x}Te_x alloy films with tellurium content up to 5 at.%. Te increases the spectral sensitivity in the red spectral region but reduces the charge acceptance and increases the dark decay rate. If one uses a Se₉₅Te₅ photo-receptors, and only one transport layer, and include a photo-generation layer of Se₈₇Te₁₃ combined with Se/Se₈₇Te₁₃ multilayers on top of the structure, a fast photo-induced discharge under illumination not only with $\lambda = 750$ nm but also with $\lambda = 800$ nm and even at $\lambda = 925$ nm can be observed. The sensitivity at 750 nm is higher than that of As₂Se₃ photo-receptor and two times higher than that of a-Si:H photo-receptors for $\lambda = 800$ nm. The stability of selenium in nanolayer structures is considerably increased. No structural change was observed after two years from preparation.

The expansion of the spectral sensitivity toward the near-infrared region and fast photo-discharge suggest that amorphous-Se monolayer/superlattice structure would be prospective for electrophotographic and laser printer photo-receivers. The super-lattices are also of high interest for getting other optoelectronic devices and an intense research in this field already started.

Finally I want to stress that many scientific papers on the special effects in chalcogenide materials and applications have been published in Journal of Optoelectronics and Advanced Materials. The most important references for the last two years are listed below [59-109]. Some papers were reviewed by Acad. Margareta Giurgea, our beloved colleague whose anniversary will be celebrated at August 19, 2005. Long live, Professor Giurgea!

4. Conclusions

A review on the effects discovered in chalcogenide glasses and amorphous thin films has been done. The applications of these effects in optics, electronics, optoelectronics, in chemistry and sensorics, described in this review, demonstrate the importance of the chalcogenide materials. The horizons are opened for new effects and new applications, a continuous challenge of the disordered state of the solids.

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