

# AMORPHOUS CHALCOGENIDE SEMICONDUCTORS FOR SOLID STATE DOSIMETRIC SYSTEMS OF HIGH-ENERGETIC IONIZING RADIATION

Oleg Shpotyuk <sup>1),2)</sup>

The application possibilities of amorphous chalcogenide semiconductors use as radiation-sensitive elements of high-energetic ( $E > 1$  MeV) dosimetric systems are analyzed. It is shown that investigated materials are characterized by more wide region of registered absorbed doses and low temperature threshold of radiation information bleaching in comparison with well-known analogies based on coloring oxide glasses.

## 1. INTRODUCTION

Solid state dosimetric systems based on coloring oxide glasses are widely used for registration of high-energetic ionizing radiation [1,2]. They are sufficiently simple in exploitation and production, stable to influence of external actinic factors, but not allow to register absorbed doses of radiation more then  $10^5$ - $10^6$  Gy. Additional inconveniences of these materials are connected with the necessity of high-temperature annealing for restoration of initial optical properties (800-1000 K). Taking above mentioned into account and using our experimental results obtained during last 15 years [3-7], we shall analyze the possibilities of practical application of amorphous chalcogenide semiconductors (AChS), which are characterized by principally another complex of physical properties in comparison with oxide glasses [8] in industrial dosimetry of high-energetic ionizing radiation.

## 2. RESULTS AND DISCUSSION

AChS were studied for the first time by Kolomiets and Goryunova forty years ago and are known to be unique solid state materials showing the complex of "traditional" semiconducting properties [8]. At the level of atomic structure they are

---

<sup>1)</sup> Physics Institute, Pedagogical University, Al. Armii Krajowej 13/15  
42201, Częstochowa

<sup>2)</sup> Institute of Materials, Stryjska str. 202, Lviv, 290031, Ukraine

inorganic polymers characterized by short-range ordering in the displacement of the various structural groups and fragments. Thus, for example, atomic structure of amorphous trisulphide arsenic  $As_2S_3$  may be presented as network of pyramidal  $AsS_3$  units mutually connected by bridge As-S-As complexes [9]. However, the limited concentration of homopolar covalent bonds As-As and S-S (to 10-20 %) exists in  $\alpha$ - $As_2S_3$  in the framework of partially polymerized complexes  $As_4S_4$ ,  $As_4S_3$ ,  $S_2$ ,  $S_8$  and so on. These “wrong” chemical bonds are specific structural defects which essentially modify energetic spectrum of AChS near the band gap [10]. The second type of structural defects in  $\nu$ - $As_2S_3$  are so called D-centers which appear as a result of external influences of pairs of opposite charged over- (positive charge) and under-coordinated (negative charge) arsenic and sulfur atoms [9,5]. The whole process of coordination defects formation in AChS consists of acts of destruction and polymerization transformations due to the following possible variants:

- 1) electron-hole pair excitation in accordance with self-trapped exciton model [11];
- 2) excitation of single electron and hole pairs autolocalized at structural fragments called soft atomic configurations [12],
- 3) chemical bond breaking or s-electron excitation [13].

It was shown previously that coordination defects formations induced by radiation influence are considered as interconnected processes of rebonding or chemical bond switching (short-range order changes) which are followed by relaxation transformations (intermediate-range order changes) comprising a large space of the  $\alpha$ - $As_2S_3$  network from two to five coordinated spheres [10]. Thus, radiation-structural transformations in AChS are associated at the final stage by two-type changes of the defect subsystem: changes of chemical bonds distribution (relation between heteropolar and homopolar bonds) in the framework of various structural groups, as well as changes of anomalous coordinated atoms with uncompensated electric charge.

Both transformation can be experimentally studied using differential Fourier spectrometry technique of induced optical absorption or reflection in the region of 400-100  $cm^{-1}$  where main vibrational bands of AChS structural groups are located. This technique firstly applied in 1988 for photostructural investigations of  $\alpha$ - $As_2S_3$  [14] is based on determination of rebonding reactions stimulated by external factors influence. It is established [5,15] that in the case of gamma-irradiation of vitreous  $\nu$ - $As_2S_3$  structural changes are stretched in the direction of chemical bonds replacements due to the following reactions:



Obtained data show that statistical weight of reaction (1) is bigger than that of reaction (2). The following annealing causes the opposite changes in chemical bonds distribution. Hence, these structural transformations are really reversible. At the level of coordination defects, reactions (1) and (2) describe the process of  $(As_4^+; S_1^-)$

defects stabilization (the upper index means the local uncompensative electrical charge and the lower one - the atomic coordination). Only one “wrong” homopolar chemical bond (As-As) is formed during transformation reaction (1), but no “wrong” bonds in the second variant (2). The similar effect may be caused in  $\nu$ -As<sub>2</sub>S<sub>3</sub> by accelerated electrons irradiation ( $E = 2-3$  MeV,  $F=10^{16}$  cm<sup>-2</sup>).

The most sensitive to the above described radiation-induced defects formation processes in AChS are their optical, electrical and photoelectrical properties. For example, influence of <sup>60</sup>Co gamma-quanta ( $E = 1.25$  MeV) with absorbed doses  $F = 10^6-10^7$  Gy leads to the long-wave shift of  $\nu$ -As<sub>2</sub>S<sub>3</sub> fundamental optical absorption edge reaching 0.04-0.06 eV for sample thickness  $d = 1-2$  mm. When all measurements are conducted at the helium-neon laser wavelength ( $\lambda = 633$  nm) corresponding to the middle part of  $\nu$ -As<sub>2</sub>S<sub>3</sub> transmission edge and optical density  $D$  is used as controlled parameter, then the dose dependence of gamma-stimulated changes  $\Delta D/D$  is linear in the range of  $5 \times 10^5-10^7$  Gy and can be written as

$$\Delta D/D = S \lg F + A, \quad (3)$$

The parameter  $S$  in eq. (3) characterizes the sensitivity of the dosimetric systems to the radiation influence and  $A$  - is a constant.

Optical properties of AChS are stable after irradiation no less than 10 years if the temperature is smaller than the thermal bleaching threshold  $T_m$ . The  $T_m$  values are essentially dependent on chemical composition of irradiated samples: for vitreous As<sub>2</sub>S<sub>3</sub>,  $T_m = 390-400$  K and for vitreous (As<sub>2</sub>S<sub>3</sub>)<sub>0.7</sub>(Sb<sub>2</sub>S<sub>3</sub>)<sub>0.3</sub>  $T_m = 385-415$  K. After annealing with temperatures more then  $T_m$ , investigated materials can be used repeatedly. The influence of technological conditions of AChS preparation is most considerable at the first stage of gamma-irradiation when apart from the above mentioned process of coordination defects formation, the homogenization of glass network and relaxation of structural macrodefects (pores, cracks, internal stresses *etc.*) are taken place. Therefore for high precision doses registration it is advisable to carry out “idle” cycle of AChS gamma-irradiation and thermoannealing. Dosimetric characteristics of AChS are not dependent considerably on the dose power  $P$  when temperature in source cavity is not higher than 330-340 K. Fulfillment of this condition is possible when  $P < 15$  Gy/s or when total dose is collected by separate cycles with  $A = 3000-5000$  Gy supporting the temperature at the level of 310-320 K.

Constructive features and main functioning principles of AChS-based dosimetric systems are identical to such as in any other dosimeters based on the radiation-stimulated changes of optical properties [1]. AChS in the form of thin layers ( $d = 1-2$  mm) obtained by well-known “conventional” technique of thermovacuum deposition [8] can be used as radiation-sensitive elements by the same way. But they are characterized by irreversible changes of optical properties [16] and sufficiently low sensitivities ( $\sigma = 0.05-0.15$ ). Therefore thin layers previously treated by absorbed light are more perspective for practical application (Table 1). Such dosimeters operate due to combined photo-radiation effects in AChS associated with defect

recharging processes [7]. It must be noted that high values of sensitivity  $\sigma > 0.6$  are reached in  $\text{As}_2\text{Se}_3$ -based dosimeters working with steady photocurrent degradation  $\Delta\sigma_{\text{hv}}/\sigma_{\text{hv}}$  (Table 1). However, a practical application of these devices is more difficult and they have more limited range of doses to be registered. When dark electroconductivity  $\sigma$  is used as controlled parameter then  $\sigma$  value is not more than 0.06. It means that such elements are unfit for device application in industrial dosimetry of high-energetic ionizing radiation.

**Table 1.** Dosimetric characteristics of AChS.

AChS	Controlled parameter	Range of registered doses (Gy)	Sensitivity
$\text{As}_2\text{S}_3$ glass (fresh-prepared)	$\Delta D/D > 0$	$5 \cdot 10^5 - 10^7$	0.30
$\text{As}_2\text{S}_3$ glass (gamma-irradiated and annealed)	$\Delta D/D > 0$	$5 \cdot 10^5 - 10^7$	0.25
$\text{As}_2\text{Se}_3$ glass (fresh-prepared)	$\Delta\sigma/\sigma < 0$	$5 \cdot 10^3 - 5 \cdot 10^6$	0.06
	$\Delta\sigma_{\text{hv}}/\sigma_{\text{hv}} < 0$	$3 \cdot 10^5 - 2 \cdot 10^6$	0.65
$\text{As}_2\text{S}_3$ film (fresh-prepared)	$\Delta D/D > 0$	$5 \cdot 10^3 - 5 \cdot 10^6$	0.13
$\text{As}_2\text{S}_3$ film (photoexposed)	$\Delta D/D < 0$	$5 \cdot 10^3 - 3 \cdot 10^5$	0.10
$\text{As}_2\text{Se}_3$ film (fresh-prepared)	$\Delta D/D > 0$	$10^3 - 5 \cdot 10^6$	0.09
$\text{As}_2\text{S}_3$ film (photoexposed)	$\Delta D/D < 0$	$5 \cdot 10^2 - 5 \cdot 10^3$	0.10
$\text{As}_2\text{Se}_3$ glass (annealed)	$\Delta\sigma/\sigma > 0$	$7.5 \cdot 10^5 - 10^7$	1.00
	$\Delta\sigma_{\text{hv}}/\sigma_{\text{hv}} > 0$	$3 \cdot 10^5 - 5 \cdot 10^6$	0.87
$(\text{As}_2\text{Se}_3)_{0.75}(\text{Sb}_2\text{Se}_3)_{0.25}$ glass (fresh-prepared)	$\Delta\sigma/\sigma < 0$	$5 \cdot 10^5 - 5 \cdot 10^6$	0.15
	$\Delta\sigma_{\text{hv}}/\sigma_{\text{hv}} < 0$	$3 \cdot 10^5 - 2 \cdot 10^6$	0.90

## REFERENCES

- [1] Frank, M., Shtolz B.: Solid state dosimetry of ionizing radiation. Moscow: Atomizdat 1973, 247
- [2] Pikaev A.K.: Dosimetry in radiation chemistry. Moscow: Nauka 1975, 312
- [3] Shpotyuk O.I.: Temperature stability of gamma-radiation induced effects in vitreous arsenic trisulphide. Zh. Prikl. Spektroskopii 46, 1987, 1, 122-126
- [4] Shpotyuk O.I.: Gamma-induced changes of optical properties of chalcogenide vitreous semiconductors. Ukr. Fiz. Zh. 35, 1990, 10., 1545-1549

- [5] Shpotyuk O.I.: Mechanism of radiation defect formation in chalcogenide vitreous semiconductors. Vopr. Atomnoj Nauki i Techniki 1990, 1, 10-14
- [6] Matkovskii A.O., Sugak D.Yu., Ubizskii S.B., Shpotyuk O.I., Chornyj E.A., Vakiv N.M., Mokritskii V.A.: Influence of ionizing radiation on materials of electronic technique. Lvov: Swit 1994
- [7] Kornelyuk V.N., Shpotyuk O.I., Sawicki I.V., Vakiv N.M.: Influence of gamma-irradiation on photodarkened layers of chalcogenide vitreous semiconductors. Zh. Prikl. Fotogr. i Kinematogr. 34, 1989, 6, 457-460
- [8] Borisova Z.U.: Chalcogenide vitreous glasses. Leningrad: University Ed. 1983, 344
- [9] Felts A.: Amorphous and vitreous inorganic solids. Moscow: Mir 1986, 558
- [10] Elliott S.R.: A unified model for reversible photostructural effects in chalcogenide glasses. J. Non-Cryst. Solids. 81, 1986, 1, 71-98
- [11] Street R.A.: Non-radiative recombination in chalcogenide glasses. Solid State Commun. 24, 1977, 5, 363-365
- [12] Klinger M.I.: Model of electronic processes in glassy semiconductors: correlation with structural features. Solid State Commun. 45, 1983, 949-953
- [13] Matkovskii A.O., Ubizskii S.B., Shpotyuk O.I.: Role of atomic displacements in radiation-induced transformations of chalcogenide vitreous semiconductors. Fiz Tverd. Tela. 32, 1990, 6, 1790-1794
- [14] Kornelyuk V.N., Sawicki I.V., Hirunenko L.I., Shpotyuk O.I., Yaskovets I.I.: Photo-induced defect formation in chalcogenide vitreous semiconductors. Zh. Prikl. Spektroskopii. 50, 1988, 3, 444-448
- [15] Shpotyuk O.I.: On the mechanism of reversible radiation-structural transformations in chalcogenide vitreous semiconductors. Zh. Prikl. Spektroskopii. 59, 1993, 5/6, 550-553
- [16] Shvarts K.K., Shpotyuk O.I., Kornelyuk V.M., Shunin Yu.N.: Irreversible photo- and radiation-stimulated effects in amorphous layers of arsenic trisulphide. Izv. AN Latv. SSR. Ser. Fiz. i Tehn. Nauk. 1, 1990, 3-13

## **CHALKOGENKOWE PÓLPRZEWODNIKI AMORFICZNE DO SYSTEMÓW DOZYMTRYCZNYCH WYSOKOENERGETYCZNEGO PROMIENIOWANIA JONIZUJĄCEGO, NA PODSTAWIE CIAŁ STAŁYCH**

### **Streszczenie**

Analizowane są możliwości zastosowania chalkogenkowych półprzewodników amorficznych w celu podniesienia jakości czułych elementów wysokoenergetycznych ( $E > 1 \text{ MeV}$ ) systemów dozymetrycznych. Ujawniono, że badane materiały charakteryzują się bardziej szerokim zakresem rejestrowania dawek absorbowanych i niższą temperaturą progową wymazywania informacji radiacyjnej w porównaniu z dobrze znanymi analogami wytworzonymi z barwionych szkieł tlenkowych.