RADIATION-INDUCED DEGRADATION PROCESSES IN VITREOUS CHALCOGENIDE SEMICONDUCTORS: OPTICAL CHANGES

R. Golovchak

Lviv Scientific Research Institute of Materials of SRC "Carat",
202, Stryjska str., Lviv, UA-79031, Ukraine
I. Franko National University,
Dragomanov str. 50, Lviv, 79005, Ukraine

INTRODUCTION

High transmittance in the optical and IR region of spectra causes a wide application of vitreous chalcogenide semiconductors (VChS) as the elements of different optical devices [1,2]. However, a stability of the VChS optical characteristics under the influence of high-energetic ionising irradiation (E > 1 MeV) is not studied sufficiently well. The data available in the literature are, as a rule, fragmentary with a great level of ambiguities in the interpretations. In this connection, it is necessary to overview and systematise the existing results.
The investigations of radiation-induced optical effects in VChS originated from 1980th when the influence of high-energetic irradiation on the mechanical properties of chalcogenide glasses had been more or less studied [3,4]. Firstly, the radiation-stimulated optical changes in bulk VChS were reported for the traditional representatives of these materials – As-based sulpho/selenides [5-7]. Then As atoms were substituted with Ge, Sb, as well as S and Se were substituted with Te [8-13]. At present time, the IR and optical properties of many binary VChS and glasses with different deviations from stoichiometry are examined to the influence of high-energetic irradiations [8-20]. The same effects in more structurally complicated multicomponent or mixed VChS systems are investigated worse [21-25].
The optical effects stimulated by high-energetic electron, neutron and gamma irradiation will be considered in this paper for different VChS compositions obtained by the standard melt-quenching method.

OPTICAL CHANGES

It is well known, that all VChS possess the fundamental optical absorption edge in the form of exponential tail or so-called Urbach tail of absorption (see curve 0 in Fig.1) [26]. The slope of this tail is closely connected with charged point defects concentration in VChS structure [27].
Schematically all radiation-stimulated changes in this region of spectra for VChS are shown in Fig.1. As it can be seen, there are two

possible processes in the fundamental absorption edge region: 0-1 – radiation-stimulated darkening effect and 0-2 – radiation-stimulated bleaching effect. Analogous processes can be observed for the optical transmittance region: 0-4 – radiation-stimulated decreasing of transmittance and 0-3 – radiation-stimulated increasing of transmittance. The number of experimentally observed results could be described by the combination of these 4 processes. The absence of any changes in one of the regions (0-0), as well as changes in the slope of transmission characteristics, should be also taken into account to combine the whole variety of possible radiation-stimulated processes.

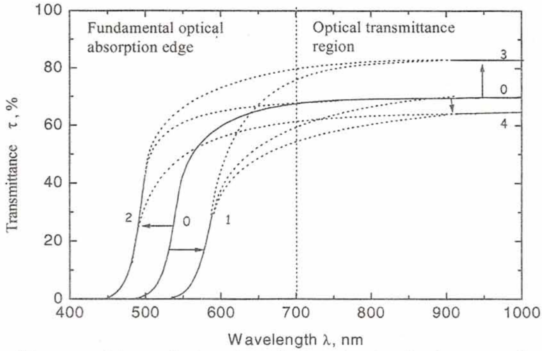

Fig.1. The possible variants of radiation-stimulated changes of optical transmission spectra in VChS systems: 0 – initial optical transmission curve, 1-3, 1-4 and 2-3, 2-4 – optical transmission curves measured after irradiation

OPTICAL CHANGES, STIMULATED BY ELECTRON IRRADIATION

The rare data on the electron-stimulated optical effects concern mostly of As- and Ge-based VChS compositions and were obtained in 80's. It was established [5,8-14], that radiation treatment of vitreous As_2S_3, As_2Se_3, As_3Se_2, $As_{40}S_{52}Se_8$ and Ge_2S_3 chalcogenide glasses with electron beam (E=1 - 4.5 MeV, fluence $P=10^{11}$-10^{13} $cm^{-2}s^{-1}$ and dose of irradiation $\Phi=10^{15}$-10^{19} cm^{-2}) led to a long-wave shift of the transmission curve in the fundamental optical absorption edge region. This process corresponds to 0-1 shift in Fig.1. The magnitude of this effect depended essentially on the chemical composition of glasses and their stoichiometry. Thus, for As_2S_3 VChS the greatest electron-induced optical effect was observed. It sufficiently decreased after As was substituted with Ge (in Ge_2S_3) as well as S was substituted with Se (in

As_2Se_3), or Se with Te [9-13]. Within of As-S and As-Se glassy systems the electron-induced optical changes increased with As content in VChS compositions [10-13]. Radiation-optical effect increased linearly also with dose of irradiation until $\Phi \sim 10^{18}$ cm^{-2}, and at greater doses reached the saturation. No detectible changes of optical characteristics were observed at $\Phi < 10^{15}$ cm^{-2} for all VChS compositions.

Additionally, the electron-induced shift of the transmission curve in the fundamental optical absorption edge region was accompanied with simultaneous slope decrease. For example, for vitreous As_2S_3 and As_2Se_3 the change in slope was evaluated as ~3 eV^{-1} at $\Phi = 10^{17}$ cm^{-2} [10]. So, it was concluded that electron irradiation at room temperatures produces the additional charged point defects, which were formed through the destruction under irradiation of chalcogen-chalcogen and As(Ge)–chalcogen chemical bonds [14]. The clusterization of the above defects with the consequent phase separation was also assumed.

The transmission decrease in the optical transmittance region was observed for all investigated VChS (0-4 process in Fig.1). The compositional and dose dependences of these changes, induced by electron-irradiation at room temperatures (~300 K), were the similar as in the case of the fundamental absorption edge region [9-11].

The interesting effect was observed when the radiation treatment was performed at the temperatures essentially lower, than the room temperature. Thus, for example, As_2S_3 irradiated at T=190-220 K revealed a relatively weaker electron-induced optical changes in the fundamental absorption edge region in comparison to the irradiated at T=300 K one [12]. At the same time, such conditions of radiation treatment led to the increasing of transmission in the optical transmittance region (0-3 process in Fig.1) on the contrary to the effect obtained at room temperature irradiation (decreasing of transmittance, 0-4 process) [12].

The electron-induced optical changes have a reversible nature. In the case of vitreous Ge_2S_3, thermal annealing (at the temperatures below the softening point T_g) completely restores the initial position of transmission curve obtained before irradiation. The other investigated VChS (As_2Se_3, As_3Se_2, $As_{40}S_{52}Se_8$) possessed a partial reversibility [9,12]. It should be mentioned that the transmittance in the fundamental optical absorption edge region restores faster than the transmittance at greater wavelengths. An increasing of the annealing temperature leads to a sharp increasing of the velocity of these restoration processes [12].

Recently, the dichroism in electron-induced optical changes was discovered for vitreous As_2S_3 [14]. It means that optical effect, induced by electron irradiation, depends essentially on the positional relationship of electron beam and sonde light beam of the spectrophotometer.

OPTICAL CHANGES, STIMULATED BY NEUTRON IRRADIATION

The neutron-stimulated optical changes are poorly investigated even for binary VChS. Only some results were obtained in the middle of 90's for vitreous As_2S_3 [7,8,16,17], $As_{40}S_{52}Se_8$ [8] and AsGeSe [16,17]. The optical changes induced by neutron irradiation (fluence $P=10^{11}$-10^{13} $cm^{-2}s^{-1}$, dose of irradiation $\Phi=10^{15}$-10^{19} cm^{-2}, transmission measurements were carried out through 3-8 moths after irradiation) are essentially greater than those, induced by electron beam. Still, the qualitative peculiarities of these changes are the similar: the long-wave shift of the transmission curve in the fundamental optical absorption edge region (0-1 process in Fig.1) and slope decrease of the latter are observed after irradiation; the 0-4 process (decrease of transmittance in optical transmittance region) is also detected. The linear increasing of the magnitude of neutron-induced optical effect with the dose of irradiation retains until the saturation at $\Phi>10^{18}$ cm^{-2} is reached. The neutron irradiation with doses less than 10^{15} cm^{-2} produces no effects on the optical VChS properties.

The additional peculiarities were obtained for neutron-stimulated optical changes in vitreous As_2S_3 and AsGeSe [16,17]. Purified waterless As_2S_3 exhibits the neutron-induced increasing of transmittance (0-3 process in Fig.1) in the wavelengths region > 1.1 μm, in objection to non-purified one. The introducing of Cu or Pb impurities (4-5 at. %) into the AsGeSe matrix does not change the tendency of these VChS to neutron-stimulated darkening effect and decreasing of transmittance in optical transmittance region.

The radiation treatment with reactor neutrons leads to general increasing of all optical losses in As_2S_3 and $As_{40}S_{52}Se_8$ fibers [7,8]. However, some additional maximums in optical loss spectra appear as a result of irradiation. The neutron-stimulated short-wave shift is observed for some of these bands. Thus, at the dose of $\Phi=10^{19}$ cm^{-2} (when the maximal neutron-induced optical losses are observed in As_2S_3 fiber), the optical loss maximum at 630 nm shifts after irradiation in the region of smaller wavelengths and restricts in shape. This feature was connected with partial crystallization of liquid phase regions created under radiation treatment (20-40 μm in dimension). The neutron-induced optical losses in As_2S_3 fiber can be partially reduced by the thermal annealing [7].

OPTICAL CHANGES, STIMULATED BY GAMMA IRRADIATION

There are many scientific works devoted to the gamma-induced effects in VChS. However, only a small part of them concerns of the optical changes in bulk chalcogenide glasses. The reason is that in the very beginning thin films objects of VChS were used for investigations of gamma-induced optical effects [6], and as a result small effects and unmatched data were obtained. Now, it is well known that these effects essentially enhance with thickness [20]. So, bulk VChS compositions are more appropriated for gamma-stimulated optical effect studies.

The influence of the gamma irradiation on the optical properties of bulk chalcogenide glasses is sufficiently studied for As-S, As-Se, As-Ge-S, As-Ge-Se, Bi-As-Se, Sb-Ge-S VChS systems [20-25]. The compositional and dose dependences for them are established. Let's consider these systems separately.

The equivalent of 0-1 process (darkening effect, see Fig.1) and slope decrease in the fundamental absorption edge region was observed after gamma irradiation (E=1.25 MeV, P=4-20 Gy/s, $\Phi=10^6$-10^9 Gy, temperature during irradiation T~300 K) for all compositions from As-S, As-Se, As-Ge-S, As-Ge-Se, Sb-Ge-S VChS systems [20-24]. The value and the character of this long-wave shift depend essentially on the chemical composition of VChS, their stoichiometry, thickness, as well as on the dose of irradiation.

The recent investigations show additionally a great importance of the temperature during gamma treatment and the period of natural storage before measurements. The latter is important owing to the discovered non-stability under the natural conditions of gamma-induced changes [23]. In this connection the total radiation-optical effect should be divided into two components: dynamic (gradually damping during 2-3 months of natural storage) and static (remaining to be a constant for a long period of time). Unfortunately, this circumstance was not taken into account in earlier researches, which resulted in bed agreement of the experimental data, obtained by various authors.

The next regularities of the gamma-induced optical changes (static component of the effect) in fundamental absorption edge region follow from the available results:

the magnitude of the gamma-stimulated changes in binary VChS systems increases with As content;

substitution of S atoms with Se ones leads to the decreasing of magnitude of the darkening effect;

the increasing of Ge content in pseudobinary VChS compositions results in increasing of the magnitude of static component;

the substitution of As atoms with Sb ones leads to the passivation of gamma-induced optical changes and their disappearing in VChS with high Sb concentration;

introduction of Cu or Pb impurities (even at the rate of 1 at.%) into As-Ge-Se VChS matrix completely annuls the sensitivity of above glasses to gamma radiation;
the non-stoichiometric Ge-containing ternary VChS reveal a well-expressed peculiarities (extrema) of the magnitude of gamma-induced optical changes in the vicinity of transition point from two-dimensional to three-dimensional type of glass structure;
the magnitude of radiation-optical darkening effect linearly increases with dose and go into saturation at greater Φ;
gamma-irradiation with Φ<0.5 MGy at normal conditions produces no detectible changes in VChS optical properties (that's why some researchers didn't obtain any effects in ternary As-Se-Te VChS systems [21]).
Gamma irradiation of Bi-As-Se VChS leads to specific changes in optical properties. When Bi concentration is low in the VChS composition, the gamma-induced darkening effect (0-1 process in Fig.1) is observed, while with increasing of Bi containing, the gamma-stimulated bleaching effect (0-2 process in Fig.1) takes place [25].
There are no strict rules on the gamma-induced effects in optical transmittance region of spectra for the observed VChS systems. These changes are revealed through the both transmittance increase and transmittance decrease depending on the chemical composition of VChS, their structure and stoichiometry, conditions of preparation and the parameters of irradiation (dose, temperature etc.). So, the whole variety (0-0, 0-3, 0-4) of optical processes even within of the one VChS system can be expected.
The radiation-optical effect has a reversible nature. Thermal annealing (up to the temperatures 20-30 K below the softening point T_g) completely or partially restores the initial transmission before irradiation. The ratio of such restoration depends on the structural peculiarities of the VChS.

IR IMPURITY ABSORPTION CHANGES

The application of bulk VChS in IR optics is limited by the number of impurity absorption bands in 2.5-25 μm wavelengths region corresponded to different oxide, hydroxyl and hydride complexes. However, their behaviour under the influence of high-energetic ionising irradiation is still being poor investigated.
There is no available data on the electron-induced effects in this region of spectra for VChS materials.
A few reports are devoted to the neutron-induced changes in impurity absorption spectra of vitreous As_2S_3 and AsGeSe [16,17]. Thus, it was established, that neutron irradiation with $\Phi=(1\text{-}5)\cdot10^{19}$ cm^{-2} ($P=5\cdot10^{13}$ $cm^{-2}s^{-1}$, transmission measurements were carried out 3-8 moths after

irradiation) of vitreous As_2S_3 and AsGeSe leads to the increasing of 2.86 μm impurity band (stretching vibrations of O-H complexes) for As_2S_3 and decreasing of the same band intensity for AsGeSe. The second O-H stretching vibrational band (2.76 μm) completely disappears, and the intensity of O-H (6.25 μm, in H-O-H groups) deformation vibrations essentially decreases after neutron irradiation for As_2S_3. Some absorption bands can appear in the IR impurity spectra as the result of chemical elements transmutations under the neutron irradiation. For example, the 4.95 μm impurity absorption band in vitreous As_2S_3 corresponds to the Se-H bonds, where ^{76}Se is the product of nuclei reactions. The As-O absorption band at 12.8 μm does not change after neutron treatment as in vitreous As_2S_3 as in AsGeSe. The other vibrational bands in AsGeSe (Ge-O, Se-H) shift in the long-wave region of spectra and spread.

Gamma-induced ($E=1.25$ MeV, $P=4\text{-}20$ Gy/s, $\Phi=10^6\text{-}10^9$ Gy, temperature during irradiation T~300 K) changes in IR impurity absorption spectra are well investigated for vitreous As_2S_3 and As-Ge-S, Sb-Ge-S, As-Ge-Se VChS systems [18,19,28-30]. In the strict sense, the decreasing/increasing of absorption band intensities is very slight effect and depends on many factors, such as structural peculiarities, purity of VChS samples, their amorphism, conditions of radiation treatment, thermal prehistory and so on. Generally, as a rule, the insignificant gamma-stimulated increasing of practically all impurity absorption band intensities is observed for all VChS [28-30]. However, in [18] the gamma-induced decreasing of hydroxyl O_nH_m (2.77 μm and 6.25 μm) and hydride S-H (4.2 μm) absorption band intensities in vitreous As_2S_3 is reported, while the radiation-induced changes in As-Ge-Se glasses are to be neglectfully small at all.

The correlation between gamma-induced changes in IR impurity absorption spectra and structural features, for example, is well expressed for non-stoichiometric Sb-Ge-S system, where the maximal decreasing of S-H band intensity corresponds to minimum of glass compactness [30]. The influence of other factors on the gamma-induced changes in IR impurity absorption spectra needs further investigations.

CONCLUSIONS

The known data on the influence of electron, neutron and gamma irradiation on the optical and IR properties of bulk VChS are summarized in present report. The overviewed optical effects, stimulated by different type of high-energetic ionising irradiation are assumed to have the similar nature. The ambiguities and discordance in the results, obtained by different authors, can be successfully explained by the different conditions of samples preparations, radiation treatment and post-radiation history.

REFERENCES

A.Feltz, W.Burckhardt, B.Voight, D.Linke, J. Non-Cryst. Solids 129 (1991) 31-39.
A.Seddon, J. Non-Cryst. Solids 184 (1995) 44-50.
I.A.Domorjad, D.Kajpnazarov, Izv. AN UzSSR, Phys-Mat. Sci. 3 (1964) 67-70 (in Rus).
I.A.Domorjad, in: Radiation-stimulated processes in solids, Tashkent, Fan (1969) 57-59 (in Rus).
A.V.Moskalonov, Izv. AN LatvSSR. Phys. Techn. Sci. 5 (1976) 64-69 (in Rus).
I.A.Tekucheva, I.A.Domorjad, Rjazan Radiotechnical Institute, VINITI 3.11.1982 (1982) 16 (in Rus).
A.M.Andriesh, U.A.Bykovskij, U.V.Borodakij, A.F.Kozhin, A.V.Mironos, V.L.Smirnov, V.V.Ponomar, Letters in ZhTF 10, *9* (1984) 547-549 (in Rus).
A.Ya.Vinokurov, A.N.Garkavenko, L.I.Litinskaya, A.V.Mironos, A.M.Rodin, Avtometrija 5 (1988) 28-31 (in Rus).
Sh.Sh.Sarsembinov, E.E.Abdulgafarov, M.A.Tumanov, N.A. Rogachev, J. Non-Cryst. Solids. 35-36, *2* (1980) 877-882.
Sh.Sh.Sarsembinov, Vestn. AN KazSSR *1* (1982) 55-62 (in Rus).
R.M.Guralnik, S.S.Lantratova, V.M.Lubin, Sh.Sh.Sarsembinov, Sov. Phys. Stat. Sol. 26, *12* (1982) 1334-1337.
Sh.Sh.Sarsembinov, R.M.Guralnik, in: Physics of Solid State, Alma-Ata, KazGU (1986) 12-22.
Sh.Sh.Sarsembinov, R.M.Guralnik, B.S.Zhakupbekov, U.I.Krotov, S.Ya.Maksimova, Sov. Phys and Chem. of Glasses 13, *1* (1987) 143-145.
Sh.Sh.Sarsembinov, E.E.Abdulgafarov, Vestn. AN KazSSR *5* (1981) 51-57 (in Rus).
O.I.Shpotyuk, V.O.Balitska, Phys. Stat. Sol. A165 (1998) 295-302.
L.F.Konorova, N.S.Zhdanovich, V.A.Didik, I.M.Prudnikov, Fiz. i Tehn. Poluprov. 23, *4* (1989) 706-709 (in Rus).
L.F.Konorova, N.S.Zhdanovich, Fiz. i Tehn. Poluprov. 27, *3* (1993) 470-473 (in Rus).
L.F.Konorova, T.I.Kim, N.S.Zhdanovich, M.A.Litovskiy, Sov. J. of Theor. Phys. 55, 4 (1985) 788-791.
L.F.Konorova, T.I.Kim, N.S.Zhdanovich, M.A.Litovskiy, Fiz. i Tehn. Poluprov. 21, *7* (1987) 1300-1302 (in Rus).
O.I.Shpotyuk, A.O.Matkovskii, A.P.Kovalsky, M.M.Vakiv, Rad. Effects and Defects in Solids 133, *1* (1995) 1-4.
S.A.Fayek, A.F.Maged, Mater. Sci. Eng. B32 (1995) 47-49.

A.F.Maged, K.I.Montasser, H.H.Amer, Mater. Chem. Phys. 56 (1998) 184-188.
O.I.Shpotyuk, A.P.Kovalskiy, E.Skordeva, E.Vateva, D. Arsova, R.Ya.Golovchak, M.M.Vakiv, Physica B. Condensed Matter 271 (1999) 242.
O.I.Shpotyuk, T.S.Kavetskyy, A.P.Kovalskiy, R.V.Lutsiv, V.Pamukchieva, Ukr. Phys. J. 46, *4* (2001) 495-498 (in Ukr).
A.P.Kovalskiy, Bull. of Lviv University, Phys. series 22 (1989) 85-88 (in Ukr).
A.Feltz, Amorphous and vitreous inorganic solids. Moscow, Mir, 1986, (p.556) (in Rus.).
Ya.G.Kljava, Sov. Phys. Stat. Sol. 27, *5* (1985) 1350-1353.
O.I. Shpotyuk, Ukr. Phys. J., 32 (1987) 509-512 (in Ukr).
R.Ya.Golovchak, Bull. of Lviv University, Phys. series 33 (2000) 86-91 (in Ukr).
T.S.Kavetskyy, J. of Phys. Studies 4, *3* (2000) 350-354 (in Ukr).