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Combined configuration-enthalpy model describing radiation-optical responses in chalcogenide semiconductor glasses

M. Shpotyuk[a,*], O. Shpotyuk[b,c], V. Balitska[d]

[a] Lviv Polytechnic National University, 12 Bandera Str., Lviv, 79013, Ukraine
[b] Jan Dlugosz University in Czestochowa, 13/15 al. Armii Krajowej, Czestochowa, 42-200, Poland
[c] O.G. Vlokh Institute of Physical Optics, 23 Dragomanov Str., Lviv, 79005, Ukraine
[d] Lviv State University of Life Safety, 35 Kleparivska Str., Lviv, 79007, Ukraine

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ABSTRACT

Combined configuration-enthalpy model evolving free energy configuration-coordinate and thermodynamic enthalpy diagrams is developed to describe the phenomenology of optical responses in structural metastability of chalcogenide semiconductor glasses of As-S system activated under prolonged physical ageing and high-energy γ-irradiation. The developed approach foresees glass stabilization in *ground-state multibasin* formed by *rejuvenation-induced*, *irradiation-induced* and/or most stable *annealing-induced basins*, interlinked by thermally-activated *over-barrier jumping* and *through-barrier tunneling* transitions. Effect of high-energy γ-irradiation in glasses is described due to vertical transitions of atomic sites into excited state followed by non-radiative relaxation into irradiation-induced glass ground state. This approach based on interlinked enthalpic and configuration-coordinate diagrams allows complete parameterization of optical responses related to induced metastable states, defined in *blue* (bleaching) or *red* (darkening) shifts in the transmission spectra of As-S glasses detected in the region of their fundamental optical absorption edge.

1. Introduction

Chemical compounds of chalcogens (S, Se, Te) with some elements from IV-V groups of the Periodic Table (mostly P, As, Sb, Bi, Ge, etc.) stabilized by rapid melt quenching, known as chalcogenide semiconductor glasses (ChSG), compose an important class of vitreous media for multifunctional photonics application in the vis-IR spectral region (Feltz, 1993; Adam and Zhang, 2013; Adam et al., 2015). Because of great variety of metastable states available for glassy networks with fully saturated covalent bonding (Feltz, 1993; Adam and Zhang, 2013; Adam et al., 2015; Popov et al., 2004), this unique optical functionality of ChSG can be governed, to a great extent, by external stimuli (Shpotyuk et al., 2004). At least, two aspects of this issue are worth to be mentioned in this view with reference to the famous Ovshinsky's experiments (Ovshinsky et al., 1968) in the latest 1960-s declaring remarkable radiation hardness of the ChSG-based ovonic systems near crystal-to-amorphous phase transition, and the pioneering works of Domoryad et al. (Starodubcev et al., 1961; Domoryad et al., 1963; Domoryad and Kaipnazarov, 1964) since the earliest 1960-s starting comprehensive research on radiation-structural modification (RSM) of Ge-As/Sb-S/Se ChSG possessing pronounced glass-forming ability. Noteworthy, in the known A.I. Popov's consideration (Popov et al., 1983, 1988, 2004; Popov, 2002), various levels of RSM can be activated simultaneously in these ChSG resulting in the phenomenon complexity at the interconnected levels of short- and medium-range structural ordering, morphology and defect subsystem.

Later, to clarify the phenomenology of optical responses in the metastability of ChSG, a number of free volume configuration-coordinate diagrams (CCD) was proposed taking into account specificity of irradiation treatments (Shpotyuk et al., 2004; Kolobov et al., 1981, 2001; Wu and Chen, 1986; Amin, 2001; Tanaka et al., 2009; Kolobov, 2003; Kavetskyy et al., 2008; Balitska and Shpotyuk, 2011). Thus, in case of absorbed light photoexposure (Kolobov et al., 1981, 2001; Tanaka et al., 2009), these models assumed ground state built of double-well potentials with distinct barrier separating the metastable state. The system was considered to be transferred into the metastable

Abbreviations: ChSG, chalcogenide semiconductor glasses; RSM, radiation-structural modification; CEM, configuration-enthalpy model; CCD, configuration-coordinate diagram; TED, thermodynamic enthalpic diagram; SCL, super-cooled liquid; FOAE, fundamental optical absorption edge; DPT, destruction-polymerization transformations; CTD, coordination topological defects

* Corresponding author.
E-mail address: shpotyukmy@yahoo.com (M. Shpotyuk).

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state under photoexcitation and returned back in the ground state) under thermal annealing. To explain RSM origin in case of γ-irradiation (Shpotyuk et al., 2004; Kavetskyy et al., 2008; Balitska and Shpotyuk, 2011), the CCD were developed giving some configurational snapshot of free energy E landscape including the stretched metabasins built of many tiny basins, which describe local stability of smaller atomic configurations in respect to their structure defined by generalized coordinate q. Appearance (disappearance) of structural defects, their stability (instability) in a glass matrix, thermal restoration (generation) into ground non-defective state were described within CCD due to vertical (radiative and non-radiative) excitations, as well as horizontal (over-barrier thermally-induced jumping and through-barrier tunneling) transitions (Balitska and Shpotyuk, 2011).

At the same time, the phase equilibria in ChSG under dufferent external excitations were sussesfully described exploring an approach of thermodynamic enthalpic diagram (TED), giving, in fact, the temperature variations of enthalpy, configurational entropy or free volume of a glass subsequently visiting melt, as well as super-cooled liquid (SCL), solid-crystalline and/or solid-glassy states (Struik, 1978; Saiter, 2001; Cangialosi, 2014; Kimura et al., 1981). Such approach was useful to explain not only physical ageing in ChSG (Saiter, 2001; Cangialosi, 2014), but also effects of other external influences. Thus, the known photostructural changes in thin arsenic sulphide films under absorbed light illumination at different temperatures defined by spectral positions of their fundamental optical absorption edge (FOAE) were treated by Kimura et al. (1981) as tending the amorphous system towards/backwards thermodynamic equilibrium of extrapolated SCL states. Thereby, the idea has been appeared to merge free-energy variations in ChSG walking through different configurations and thermodynamic equilibrium states within a combined model, comprising simultaneous visualization due to CCD and TED.

Such approach was applied recently in the famous presentation of Ke. Tanaka and K. Shimakawa (Tanaka and Shimakawa, 2011), who first explained the general tendencies caused by interrelation between melt liquid, SCL, glassy and crystalline states (ascribing the multiwell equilibria set for a glass and sharp-deep separate minimum for a crystal). In this work, the combined *configuration-enthalpy model* (CEM) will be develop to clarify optical responses in bulk glassy g-As-S (Shpotyuk et al., 2014) originated from their physical ageing and γ-irradiation.

2. Experimental

The studied ChSG were chosen from glass-forming region of binary As-S system to have vitreous samples sensitive to radiation-induced defects (close-to-stoichiometry compositions g-$As_{36}S_{64}$, g-$As_{40}S_{60}$, and g-$As_{42}S_{58}$ (Shpotyuk et al., 2014)) and pronounced ability to physical ageing (S-rich compositions g-$As_{33}S_{67}$ and g-$As_{30}S_{70}$ (Shpotyuk et al., 2013a)). The samples were prepared by conventional melt-quenching route from purified elemental ingredients and preliminary affected to below-T_g thermally-assisted physical ageing before being irradiated, as described in more details elsewhere (Shpotyuk et al., 2014). The γ-irradiation was carried out at the ambient conditions of high-energy ^{60}Co radiation field (1.25 MeV) with commulative absorbed dose of Φ~3.0 MGy.

The optical transmission spectra were recorded for polished disc-like samples (having thickness approaching ~1–1.5 mm) in the region of their FOAE in few days after γ-irradiation finishing and one month later (to exclude dynamic post-irradiation decaying component (Shpotyuk et al., 2004)). Thereby, the *in-situ* backward-chronology approach (Shpotyuk et al., 2017, 2018) was utilized for γ-irradiated g-As-S samples (which are nominated to be in *irr*-state) under their subsequent transition towards post-irradiation near-T_g annealed state (*ann*-state, i.e. for most physically aged samples) and rejuvenated state (*rej*-state, i.e. for annealed samples affected to renovation procedure due to over-T_g heating and cooling with the same rate).

3. Results and discussion

The first step in the identification of radiation-optical response consists in comparative analysis of the recorded optical transmission spectra in the region of FOAE for non-irradiated thermally-aged and rejuvenated g-As-S samples with those recorded for γ-irradiated ones. Originally, this comparison was performed owing to *in-situ* experiments arrasnged for γ-irradiated (with ~3.0 MGy absorbed dose) stoichiometric g-$As_{40}S_{60}$ (equivalent of g-As_2S_3) affected to near-T_g thermal annealing just in the spectrophotometer chamber (Shpotyuk et al., 2013b). The observed short-wave shift in the detected transmission spectra for irradiated g-$As_{40}S_{60}$ (alternatively, the blue shift or bleaching) was attributed to thermally-induced destruction-polymerization transformations (DPT) related, in part, to disappearing of coordination topological defects (CTD) in fully saturated covalent-bonded glass network (Shpotyuk et al., 2004). The total γ-induced effect was also compared with static one (which remains in ChSG after relaxation of quick dynamic changes) due to *ex-situ* measurements for g-As_2S_3-Sb_2S_3 (Shpotyuk and Polovynko, 2013). The observed long-wave shift in the FOAE spectra in γ-irradiated ChSG (red shift or darkening) ascribed to radiation-induced generation of CTD unprecendently testifies on more unfavorable *irr*-state for them with correspondingly most deeply-maintained local minimum of free energy basin.

The second step concerns comparison of γ-induced optical effects in g-As-S with those caused by their subsequent thermal annealing and rejuvenation, this analysis being performed due to *in-situ* measurements for ChSG possessing high propensity to radiation-induced DPT (such as g-As_2S_3) or physical ageing (such as g-AsS_2) (Shpotyuk and Shpotyuk, 2013). It was shown that γ-irradiation led to the darkening of stoichiometric g-As_2S_3, while no changes were observed in S-rich g-AsS_2. In contrast, the rejuvenation procedure applied to the annealed samples led to red shift of their FOAE whichever the glass composition. Hence, thermal annealing occurs destructive effect on *irr*-state (due to lower-maintained free energy basin corresponding to *ann*-state), which can be further destroyed by rejuvenation, i.e. returning the annealed ChSG to non-aged *rej*-state with higher-maintained local free energy basin.

In final, to clarify optical responses in g-As-S, the third step should be realized, this being performed for the same γ-irradiated samples as compared with those taken after subsequent *in-situ* cycles of near-T_g annealing and rejuvenation (Shpotyuk et al., 2014).

The corresponding changes in the FOAE of the studied g-As-S samples are depicted on Fig. 1. It is seen that red (long-wave) shift of the FOAE prefers after γ-irradiation in g-As_2S_3 (see Fig. 1b), so that any deviations from stoichiometry towards S- or As-rich compositions reduce γ-induced darkening. For S-rich samples rejuvenated after γ-irradiation, the bleaching effect is anticipated as result of γ-assisted physical ageing (not CTD formation). Difference in spectral positions of FOAE for g-As-S in *ann*-state and *rej*-state confirms this conclusion, showing evident bleaching resulting from thermally-induced physical aging for rejuvenated samples on Fig. 1. Thus, the γ-induced changes in the FOAE can be considered as resulting from balance of two competitive processes, these being DPT (including CTD formation (Shpotyuk et al., 2004)) and physical ageing enhanced under prolonged γ-irradiation at the ambient conditions (Shpotyuk et al., 2013a).

These data allow positioning the principal features of these changes in combined CEM describing externally-induced metastability in the ChSG as shown on Fig. 2.

The left part of this model represents multiwell CCD for different local free-energy basins of *ground glass-state metabasin* formed by *irr*-state, deeply physically aged or *ann*-state and *rej*-state wells, and *ground crystal-state basin* formed by deepest crystalline well. The right part of CEM gives enthalpy levels for ChSG in strict respect to their CCD states, along with thermodynamic levels ascribed to melt, SCL or crystal.

The ordinate of sattle point for each basin (which can be approximated by quasi-parabola for small deviations in local coordinate q (Kolobov et al., 2001; Tanaka et al., 2009)) plays decisive role in the

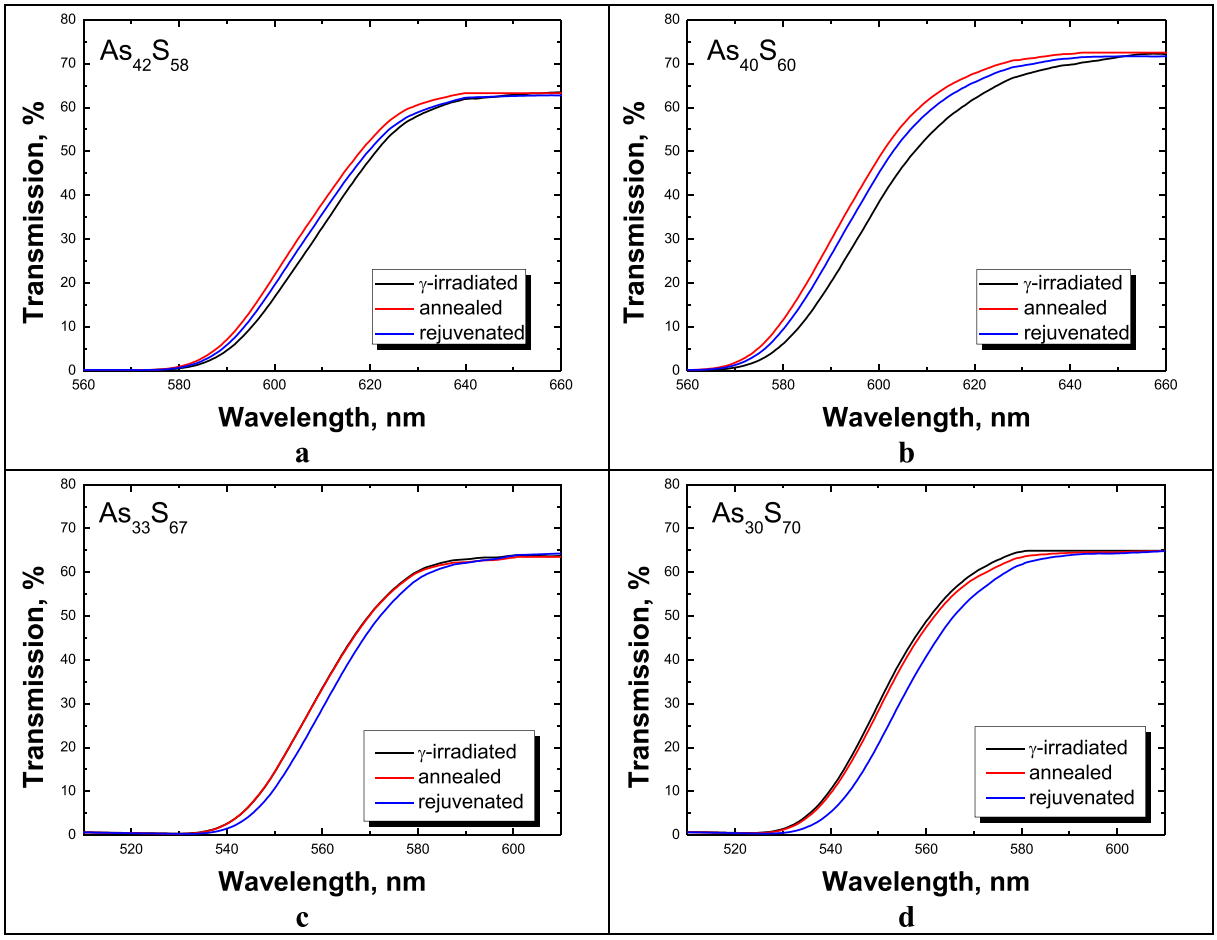

Fig. 1. Optical transmission spectra detected in backward *in-situ* chronology for g-$As_{42}S_{58}$ (a), g-$As_{40}S_{60}$ (b), g-$As_{33}S_{67}$ (c) and g-$As_{30}S_{70}$ (d) glasses in subsequent cycles of γ-irradiated (black curve), near-T_g annealed (red curve) and rejuvenated (blue curve) states. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

spectral position of the FOAE (left part on Fig. 2) and its thermodynamics metastability (right part on Fig. 2). In respect to obvious difference in the FOAE for g-As-S detected *in-situ* for three subsequent states (irradiated, irradiated-and-annealed, irradiated-and-annealed-and-rejuvenated, Fig. 1), the lower-maintained ground glass-state basin on Fig. 2 corresponds to physically aged ChSG (being in *ann*-state), while *irr*-state entirely belongs to the upper glass-state basin (hence, *rej*-state basin fits in the intermediate position between *ann*-state and *irr*-state ones). So relation between enthalpy levels on right-sided TED on Fig. 2 reflects upwards changes as indicative of red shift in the FOAE (darkening effect) and downwards changes as indicative of blue shift (bleaching effect).

The *over-barrier jumping* transitions occur between different ground glass-state basins on Fig. 2 (left part) being activated by thermal

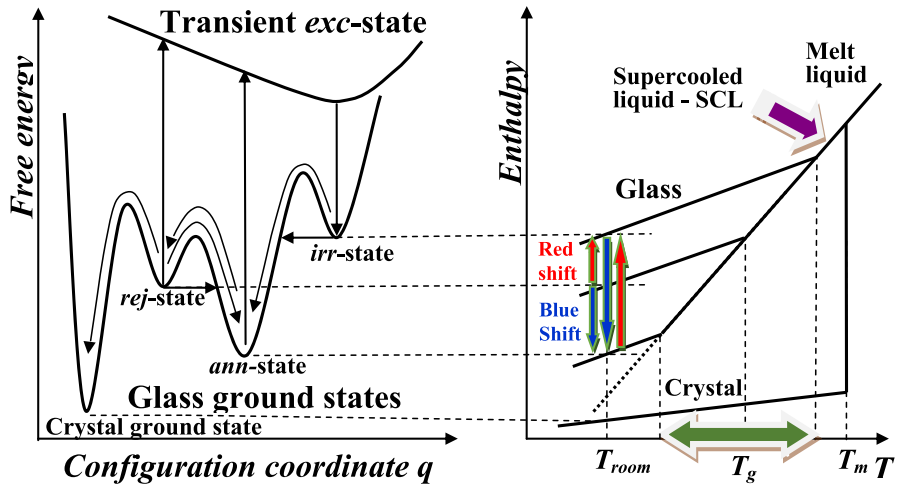

Fig. 2. Combined CEM for externally-induced metastability in ChSG.

anneling, describing bleaching of the rejuvenated ChSG under prolonged thermally-assisted ageing and, vise versa, darkrning of the aged ChSG affected to rejuvenation procedure (Shpotyuk et al., 2013a; Golovchak et al., 2010), as well as bleaching of the irradiated ChSG under above-threshold thermal annealing (Shpotyuk et al., 2004; Shpotyuk et al., 2013a; Shpotyuk. et al., 2005). In contrast, the *through-barrier tunneling* transitions between ground glass-state basins on Fig. 2 are ascribed only to bleaching effects caused by physical ageing in the rejuvenated (*rej*-to-*ann* state transition) or irradiated ChSG (*irr*-to-*ann* state transition) under ambient conditions (Shpotyuk et al., 2013a; Golovchak et al., 2005).

The population of *irr*-state can be enhanced only through vertical transitions employing transient excitation-induced state (*exc*-state) as shown in CCD on Fig. 2. Thus, direct excitation of both lowest ground glass-state basins (equivalent to the ChSG in *ann*-state or *rej*-state) by above-bandgap irradiation (for instance, by high-energy γ-quanta or absorbed light photoexposure) followed by non-radiative relaxation into *irr*-state results in pronounced red shift of the FOAE, in good harmony with known data (Shpotyuk et al., 2013a; Golovchak et al., 2010).

Balance between relaxation processes possible in the ChSG within this combined CEM can be described analitycally using the known formalism of unified CCD (Balitska and Shpotyuk, 2011).

Let's denote the basins for *rej*-, *ann*- and *irr*-states as *R*, *A* and *I*, respectively, as well as the basin for excited state as *E*. For simplicity reason, the equilibrium state of crystal can be excluded from consideration due to impossibility of transitions to this state without melting. The total number *N* of atomic sites in ChSG available for externally-induced changes is composed of populations of all metastable glass-state basins and excited state basin:

$$N = N_R + N_A + N_I + N_E, \tag{1}$$

the latter term being nonzero only under continuing irradiation.

As it was assumed in (Tanaka, 1986), the llifetimes $\tau_{(R,A,I)}$ of atomic sites in metastable glass-state basins *R*, *A* and/or *I* are determined by thermally-activated transitions into

more stable state over corresponding energetic barrier $\Delta E_{(R,A,I)}$

$$\tau_S^{-1} = \nu_s \exp(-\Delta E_{(\mathrm{R,A,I})}/KT) \tag{2}$$

where ν_S is used to denote "attempt" frequency (that is frequency of site vibrations in a well). Correspondingly, the rate of such thermally-activated transitions can be determined as:

$$\frac{dN_{(R,A,I)}}{dt} = -\frac{N_{(R,A,I)}}{\tau_{(R,A,I)}} \tag{3}$$

The rate of vertical transitions from ground glass-state basins *R*, *A* or *I* to *exc*-state basin *E* depends on γ-quanta flux *Q* and materials-related absorption cross-section from the corresponding basin $\sigma_{(R,A,I)}$:

$$\frac{dN_{(R,A,I)}}{dt} = -Q\sigma_{(R,A,I)}N_{(R,A,I)} \tag{4}$$

In a similar manner, the radiative vertical transition of atomic sites from *exc*-state to *irr*-state is dependent on materials-related recombination rate k_r as

$$\frac{dN_E}{dt} = K_r N_E \tag{5}$$

Thus, a set of differential rate equations describing populations of ground glass-state basins in ChSG affected to physical ageing and γ-irradiation can be writted as follows:

$$\begin{cases} \frac{dN_R}{dt} = -\frac{N_R}{\tau_R} - Q\sigma_R N_R, \\ \frac{dN_A}{dt} = -\frac{N_R}{\tau_R} + \frac{N_I}{\tau_I} - Q\sigma_A N_A, \\ \frac{dN_I}{dt} = -\frac{N_I}{\tau_I} - Q\sigma_I N_I + K_r N_E \end{cases} \tag{6}$$

The system of above differential equation (6) allows description of kinetics of relaxation processes in ChSG within metastable glass-state basins, particularly natural, thermo- and γ-induced physical ageing, γ-induced DPT and thermal rejuvenation. The real balance of these equations depends on the ChSG specificity (due to parameters related to glass composition and thermal pre-history), as well as the parameters of exciting irradiation.

Noreworthy, the combined CEM gives good explanation not only for simple effects caused in ChSG by separate external influences, but also for complex effects caused by simultaneous or subseqent acting of several factors, such as irradiation-accelarated (Shpotyuk et al., 2013a; Shpotyuk and Golovchak, 2006; Golovchak et al., 2006) or light-assisted ageing (Shpotyuk et al., 2013a; Kozdras et al., 2007, 2011). In case of combined externally-induced influences, the last transition occurs to be decisive in the final metastability of ChSG. Thus, the *rej*-state is most energetically unfavorable among all possible thermally-activated states. So, in final, each thermal treatment provides the ChSG towards most equilibrium *ann*-state, while to visit the *irr*-state, which is most energetically unfavorable among all local basins forming ground glass-state metabasin, the more essential DPT employing *exc*-state should be activated.

4. Conclusions

The unified configuration-enthalpy model consisted of configuration-coordinate and thermodynamic enthalpy diagrams is developed to describe the phenomenology of optical responses in structural metastability of chalcogenide semiconductor glasses of As-S system activated under combined influences of physical ageing and high-energy γ-irradiation.

The model foresees glass stabilization in the multibasin of ground state formed by rejuvenation-, irradiation- and/or most stable annealing-induced basins, interlinked by thermally-activated over-barrier jumping and through-barrier tunneling transitions. Effect of high-energy γ-irradiation is reflected in vertical transitions of atomic sites into excited state followed by non-radiative relaxation in irradiation-induced ground state. The developed thermodynamic enthalpy diagram conjugated with configuration-coordinate one allows complete parameterization of corresponding optical responses related to these states, defined in blue (bleaching) or red (darkening) shifts in the transmission spectra of As-S glasses detected in the fundamental optical absorption edge region.

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