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## A unified configuration-coordinate model of structural metastability in amorphous chalcogenide glasses

## Valentina Balitska<sup>1,2</sup> and Oleh Shpotyuk<sup>\*,1,3</sup>

<sup>1</sup> Lviv Institute of Materials, SRC "Carat", 202, Stryjska Str., 79031 Lviv, Ukraine

<sup>2</sup> State University of Vital Activity Safety, 35, Kleparivska Str., 79007 Lviv, Ukraine

<sup>3</sup> Institute of Physics, Jan Dlugosz University, 13/15, al. Armii Krajowej, 42201 Czestochowa, Poland

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\* Corresponding author: e-mail shpotyuk@novas.lviv.ua, Phone: +38 032 2638303

The unified configuration-coordinate model, describing externally-induced structural transformations in amorphous chalcogenide semiconductors, was developed. Within this model, the existing structural units of glassforming matrix are supposed to be in one of three possible states: the ground (most thermodynamically equilibrium), excited (transient) and structurally-modified (metastable) states, interconnected with a system of vertical (radiative or non-radiative) and thermally-activated overbarrier tunnelling transitions. This model is used to describe kinetics of induced metastability in amorphous chalcogenides.

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1 Introduction Amorphous chalcogenide semiconductors (AChS) firstly studied by N.A. Goryunova and B.T. Kolomiets more than five decades ago [1] are known to be unique disordered materials possessing high sensitivity to external factors. As an example, the phenomena of photo- and radiation-induced structural transformations, observed since the early 60-s [2], have been put in a ground for AChS-based sensors, optical and electrical memory switching devices, information storage and transforming systems [3,4]. It is supposed this unique ability is proper to AChS owing to high flexibility of glassy backbone with low-coordinated atoms having only two covalent-linked neighbors (two-fold coordinated chalcogen S, Se or Te atoms); relatively large content of free volume frozen near glass transition as additional volume excess over isocompositional extrapolated supercooled liquid and thermodynamically equilibrium crystal; as well as specific lone-pair character of electronic states of chalcogen atoms localized near top of a valence band as most sensitive channel for externally-activated band-band excitations [5].

At the same time, the number of parasitic degradation structural transformations caused by relaxation towards thermodynamic equilibrium is a serious obstacle for highreliable AChS-based electronics. These time-instability effects can be revealed in physical properties of AChS at normal conditions of their exploitation, this process being defined as natural physical ageing [6,7]. Under simultaneous influence of additional external factors such as high-energy irradiation, thermal or absorbed light exposure, this process occurs too as externally-induced physical ageing, the phenomenon extensively studied in the last years [8].

The above effects clearly show a so-called structural metastability proper to amorphous solids like AChS [5,8]. In spite of complicity, the great number of models was proposed to explain the microstructural origin of these effects [8,9]. From practical point, the phenomenological description of these instability-related effects is also of higher importance, especially when the final state of structural relaxation is achieved under an influence of a few acting factors, sometimes of principally different natures.

Among known phenomenological models describing metastability in AChS, the configuration-coordinate models (CCM) [8,10-14], which consider all kinds of possible interstate transitions within an energetic diagram evolving ground, transient and metastable states have an undoubted preference. Within this model, the time-instability in AChS



can be described as a system of externally-activated radiative and non-radiative transitions followed by corresponding relaxation towards thermodynamic equilibrium. In such a way, the known photoinduced phenomena (both darkening and bleaching, scalar and vector, static and dynamic), their thermal and photo-induced erasing, etc. were simply explained in thin AChS films in dependence on their chemical composition [5,9]. However, the CCM developed did not take into account the accompanied processes of physical ageing proper to AChS, and more complicated changes caused by simultaneous multifactor influences such as photo-thermally-induced, radiation-thermally-induced and photo-radiation-induced effects [8], some of them causing the opposite transformations.

**2** Generalized CCM describing metastability in AChS The generalized CCM shown in Fig. 1 involves both native- and metastable-related structural states in AChS. Within this model, all types of externally-induced effects can be divided on two main groups, direct underirradiation or transient *in-situ* effects and post-irradiation *ex-situ* ones. The latter is also known as post-irradiation physical ageing, they occurring at ambient (natural physical ageing) or thermal restoration conditions (thermallyinduced physical ageing).



**Figure 1** A unified configuration-coordinate diagram describing metastability-related effects in AChS.

The first element of this model is associated with ground or initial structural state of AChS, representing itself as multiwell quasi-parabola (Fig. 1). The deepest state within quasi-parabola X corresponds to the most stable atomic equilibrium of glass-forming network. This state can be occupied by atoms in local configurations appeared during very prolonged physical ageing under natural conditions. This process tending sometimes more than a few decades [15-17] occurs through long-term structural shrinkage of glassy backbone to eliminate additional free vol-

ume associated with its non-optimized under-constrained nature.

The higher ground states Y,  $Z_1$ ,  $Z_2$ , are characterized by more shallow potential wells, the inter-well transitions between them being thermally activated. The kinetics of these transitions is supposed to be well described by overbarrier tunneling [10]. In normal conditions, the  $Z_1$ ,  $Z_2$ ,... sub-states are unstable, being characterized by relatively low energetic barrier close to  $\sim kT$ .

The over-barrier  $Z_2 \rightarrow Z_1 \rightarrow Y$  transition corresponds to short-term physical ageing. This process occurs, in part, due to twisting of chalcogen atoms followed by structural (twisting-related) shrinkage of glassy network, while the over-barrier transition from Y into X state is associated with a more prolonged (a so-called long-term) physical ageing [17].

The second element of the proposed CCM corresponds to the excited sate U (Fig. 1), it being transient from ground and metastable ones. This state can be presented by single parabola with wide-stretched edges in accordance to strong electron-phonon coupling proper to covalentbonded AChS networks [5]. It should be noted this shortterm state is always single-well, despite a variety of external influences applied to AChS. Only vertical radiationinduced Frank-Condon-type transitions with  $E_{XU}$ ,  $E_{YU}$  and  $E_{ZU}$  energies are possible between ground X, Y, Z sub-states and excited U state. The bottom transitions  $E_{XU}$  and  $E_{YU}$  $(E_{XU} \approx E_{YU})$  are responsible for photoluminescence excitation. Such effects are accompanied by structural relaxation with corresponding changes of atomic configurational coordinate q, the difference in excitation  $E_{XU}$  ( $E_{YU}$ ) and recombination  $E^*_{UX} \approx E^*_{UY}$  energies corresponding to Stocks shift [5]. In AChS of stoichiometric  $P_2C_3$  composition (the P symbol corresponds to three-fold coordinated pnictide atom and C corresponds to two-fold coordinated chalcogen atom, respectively), this state is associated with excited  $(P_3^0; C_2^0)^*$  pair (the subscript in atomic state denotes local coordination, while the superscript is used to mark the excess of electric charge) owing to localization of unpaired electrons on each under-coordinated atom of initial heteropolar *P*–*C* covalent bond (see Fig. 2). Thus, the interband (band-to-band)  $X \rightarrow U$  transition followed by downwards  $U \Longrightarrow U^{0}$  tending describes the main channel of excitation, while  $Z_2$ ,  $Z_1$ ,  $Y \to U \Longrightarrow U^0$  transition is related to alternative channel. In contrast, the backward  $U^0 \rightarrow X \Longrightarrow X^0$  and  $U^0 \rightarrow Y \Longrightarrow Y^0$  transitions correspond respectively to radia-

The third element of the developed CCM, which is associated with metastable state ( $V_1$ ,  $V_2$ , W, ...), is a parabolic-shaped curve crossing with both excited U and ground-state X parabolas in B and A points, respectively. It splits into 3 (or even more) parabolic-like sub-states in respect to different types of possible coordinate topological defects (CTD) shown in Fig. 2. The state  $V_1$  corresponds to

tive recombination in X(Y) states.

conjugated pair (CP) of  $(P_2^+; C_1^-)$  type (alternatively, the intimate valence alternative pair), the state  $V_2$  corresponds to  $(P_4^+; C_1^-)$  CP, while the state W corresponds to random pair (RP) of  $(P_4^+; C_1^-)$  type (alternatively, the valence alternative pair).



**Figure 2** Coordination topological defects interplay in AChS exemplified by stoichiometric  $P_2C_3$  glasses.

Because CTD in  $V_1$  state are characterized by very short lifetimes, the following transitions become possible: if  $\Delta E_{V_1B} \ge \Delta E_{V_1A} \approx kT$ , the  $(P_2^+; C_1^-)$  CP transform towards A point into  $V_2$  or X states; if  $\Delta E_{V_1B} << \Delta E_{V_1A} \approx kT$ , the  $(P_2^+; C_1^-)$  CP turns back through B point into U state. In both cases, the destroyed covalent chemical bond will renew, the corresponding relaxation process attaining a monomolecular (threshold-type) behavior.

The  $V_2$  state decays though A point into X state or, alternatively, into W state, provided  $\Delta E_{V_2A} \approx \Delta E_{V_2W} \approx kT$ . In the first case, the inverse  $P - \rightarrow P - C$  bond switching followed by spontaneous  $(P_4^+; C_1^-)$  CP annihilation occurs, while the bond-conserving  $P - C \rightarrow P - P$  switching followed by  $(P_4^+; C_1^-)$  RP appearance takes place in the second case. The both processes are described by bimolecular relaxation kinetics [8].

In full respect to the above CCM, we propose a set of differential equations describing dynamic balance of possible relaxation processes in AChS. Let's denote the atomic site concentrations in X, Y, U,  $V_1$ ,  $V_2$  and W states as  $N_{state}$  (the *state* subscript denotes corresponding structural state of AhCS), photon flux as Q and cross-section of photon absorption from corresponding structural state as  $\sigma_{state}$ .

Then, the rate equation for atomic sites localized in the ground *X* state can be presented as follows:

$$\frac{dN_{X}}{dt} = \frac{N_{Y}}{\tau_{YX}} - Q\sigma_{X}N_{X} + k_{r}^{UX}N_{U} + \frac{N_{V_{1}}\left(1 - P_{V_{2}}^{A}\right)}{\tau_{V_{1}A}\left(1 - Q\sigma_{V_{2}}\left(1 - P_{V_{2}}^{A}\right)\right)},$$
(1)

where  $k_r^{UX}$  is recombination rate for radiative transition from U into X state,  $P_{V_2}^{A}$  is splitting probability for relaxation fluxes between X and  $V_2$  states in A point,  $\tau_{YX}$  and  $\tau_{V_1A}$  are lifetimes of atomic sites in Y and  $V_I$  states, respectively.

As it was shown earlier [10], the lifetimes of atomic centers localized in any metastable state was determined by thermal transition into more stable state over corresponding energetic barrier  $\Delta E$ . Hence, the lifetime of atomic centers in *Y* state,  $\tau_{YX}$ , which determines transitions into *X* state over energetic barrier  $\Delta E_{YX}$ , can be estimated as:

$$\tau_{YX}^{-1} = v_{YX} \exp\left(-\frac{\Delta E_{YX}}{kT}\right),\tag{2}$$

where  $v_{YX}$  is a so-called "attempt" frequency (the value which is of order of the frequency of vibrations in the well).

In a similar manner, the lifetime of atomic centers in CP-related  $V_1$  state, which determines thermal transition into  $V_2$  state over energetic barrier  $\Delta E_{v,4}$  is equal to:

$$\tau_{V_{1A}}^{-1} = v_{V_{1A}} \exp\left(-\frac{\Delta E_{V_{1A}}}{kT}\right),$$
(3)

where  $V_{V_1A}$  is corresponding "attempt" frequency.

In the Eq. (1), the first, third and fourth terms correspond to relaxation of atomic centers into X state from Y, U,  $V_1$  and  $V_2$  ones, respectively, while the second term describes the capture of atomic centers from X into excited U state.

In a same way, the rate equation describing atomic sites balance in sub-ground *Y* state, can be determined as:

$$\frac{dN_{Y}}{dt} = \frac{N_{Z_{1}}}{\tau_{Z_{1}Y}} - Q\sigma_{Y}N_{Y} - \frac{N_{Y}}{\tau_{YX}}, \qquad (4)$$

where  $\tau_{Z_1Y}$  is lifetime of atomic sites in  $Z_1$  state defined like (2) or (3).

The first term in the above Eq. (4) corresponds to relaxation of atomic centers from  $Z_I$  into Y state, while the second and third ones correspond to capture of atomic centers into excited U and ground X states, respectively.

The rate equation describing atomic sites in sub-ground  $Z_1$  state can be presented as:

$$\frac{dN_{Z_1}}{dt} = \frac{N_{Z_2}}{\tau_{Z_1,Z_1}} - Q\sigma_{Z_1}N_{Z_1} - \frac{N_{Z_1}}{\tau_{Z_1,Y}},$$
(5)

where  $\tau_{Z_2Z_1}$  is lifetime of atomic sites in  $Z_2$  state.



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Thus, the first term in Eq. (5) corresponds to relaxation of atomic centers into  $Z_2$  state from  $Z_1$  state, while the second and third ones correspond to capture of atomic centers into excited U and sub-ground Y states, respectively.

The rate equation describing atomic sites in the excited state U can be presented as:

$$\frac{dN_{U}}{dt} = Q\left(\sigma_{x}N_{x} + \sigma_{y}N_{y} + \sigma_{z_{1}}N_{z_{1}} + \sigma_{z_{2}}N_{z_{2}}\right) - k_{r}^{UX}N - \frac{N_{U}}{\tau_{UB}} + \frac{N_{U}\left(1 - P_{V_{1}}^{B}\right)}{\tau_{UB}\left(1 - Q\sigma_{V_{1}}\left(1 - P_{V_{1}}^{B}\right)\right)} + \frac{N_{V_{1}}}{\tau_{V,U}}$$
(6)

where  $\tau_{UB}$ ,  $\tau_{V_1U}$  are lifetimes of atomic sites in U and  $V_I$  states, respectively,  $P_{V_1}^B$  is probability for upper relaxation fluxes in B point towards  $V_I$  state.

The first, fourth and fifth terms in Eq. (6) correspond to capture of atomic centers into U state from all groundrelated (X, Y,  $Z_1$ ,  $Z_2$ ) states and metastable  $V_1$  state, while the second and third terms describe relaxation of atomic centers from U state into X and  $V_1$  ones, respectively.

The equation describing atomic sites in metastable CP-related  $V_l$  state can be given as:

$$\frac{dN_{V_1}}{dt} = \frac{N_U}{\tau_{UB}} - \frac{N_{V_1}}{\tau_{V_1A}} - \sigma_{V_1}QN_{V_1} + \frac{N_U P_{V_1}^B}{\tau_{UB} (1 - \sigma_{V_1} Q P_{V_1}^B)} - \frac{N_{V_1}}{\tau_{V_1B}}, \quad (7)$$

where  $\tau_{V_1A}$   $\tau_{V_1B}$  are lifetimes of atomic sites in  $V_I$  state.

The first and fourth terms of Eq. (7) correspond to capture of atomic centers from U state, while the second and third terms correspond to relaxation of atomic centers into X and  $V_2$  states, respectively.

The equation describing atomic sites in metastable CP-related  $V_2$  state can be written as:

$$\frac{dN_{V_2}}{dt} = \frac{N_{V_1} P_{V_2}^A}{\tau_{V_1 A} \left(1 - \sigma_{V_2} Q P_{V_2}^A\right)} - \frac{N_{V_2}}{\tau_{V_2 W}} - \frac{N_{V_2}}{\tau_{V_2 A}} , \qquad (8)$$

where  $\tau_{V_2W}$  and  $\tau_{V_2A}$  correspond to lifetimes of atomic sites in  $V_2$  state.

Finally, the equation describing atomic sites in RP-related *W* state can be given as:

$$\frac{dN_W}{dt} = \frac{N_{V_2}}{\tau_{V_2W}} \,. \tag{9}$$

Thus, the systems of proposed differential equations allow to described the formation kinetics of induced metastable states in AChS, both CTD-related and non-defect ones. The real balance of these equations depends on AChS specificity, their chemical composition and thermal prehistory, in the first hand. **3 Conclusion** The universal CCM describing induced structural transformations in AChS was developed. The model can be used to adequately describe the known induced phenomena such as:

- time instability during physical ageing of AChS in normal conditions before and after irradiation;

 dose dependences of radiation-induced optical changes, caused by corresponding CTD formation (both CP and RP type);

thermal relaxation during additional temperature treatment of the irradiated AChS;

- combined induced effects owing to simultaneous multifactor external influences (such as photo-thermallyinduced, radiation-thermally-induced, photo-radiationinduced, etc.).

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## References

- N. A. Goryunova and B. T. Kolomiets, Izv. AN USSR, Ser. Fiz. 20, 1496 (1956).
- [2] I. A. Domoryad, D. Kipnazarov, and L. Hiznichenko, Izv. AN UzSSR, Ser. Fiz.-Mater. Sci. 5, 87 (1963).
- [3] X. Zhang, H. Ma, and J. Lucas, JOAM 5, 1327 (2003).
- [4] J. S. Sanghera and I. D. Aggarwal, J. Non-Cryst. Solids 256/257, 6 (1999).
- [5] A. Feltz, Amorphous and Vitreous Inorganic Solids (Mir Moscow, 1986), p. 556.
- [6] R. Golovchak, A. Kozdras, and O. I. Shpotyuk, Solid State Commun. 145, 423 (2005).
- [7] J.-M. Saiter, J. Optoelectron. Adv. Mater. 3, 685 (2001).
- [8] O. Shpotyuk, Radiation-induced effects in chalcogenide vitreous semiconductors, in: Semiconducting Chalcogenide Glass 1: Glass Formation, Structure, and Simulated Transformations in Chalcogenide Glassess, edited by R. Fairman and B. Ushkov (Elsevier Academic Press, 2004).
- [9] S. Elliott, J. Non-Cryst. Solids 81, 71 (1986).
- [10] K. Tanaka, Jpn. J. Appl. Phys. 25, 779 (1986).
- [11] A. V. Kolobov and O. V. Konstantinov, Philos. Mag. B 47, 1 (1983).
- [12] G. A. M. Amin, Phys. Chem. Solids 62, 921 (2001).
- [13] R. A. Street, Solid State Commun. 24, 363 (1977).
- [14] N. Toyosawa and K. Tanaka, Solid State Commun. 97, 623 (1986).
- [15] J.-M. Saiter, M. Arnoult, and J. Grenet, Phys. B 355, 370 (2005).
- [16] R. Golovchak, O. Shpotyuk, A. Kozdras, M. Vlcek, B. Bureau, A. Kovaslkiy, and H. Jain, J. Phys.: Condens. Matter 20, 245101 (2008).
- [17] R. Ya. Golovchak, A. Kozdras, and O. I. Shpotyuk, Solid State Commun. 145, 423 (2008).