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

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The unified configuration-coordinate model, describing externally-induced structural transformations in amorphous chalcogenide semiconductors, was developed. Within this model, the structural units of glass-forming matrix are supposed to be in one of the next three states: ground (the most thermodynamically equilibrium state), excited (the transient state) and structurally-modified (the metastable state) ones, interconnected with a system of vertical radiative (non-radiative) and thermally-activated over-barrier tunnelling transitions.

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1. Introduction: on the phenomenology of structural instability in amorphous solids

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 extremely high sensitivity to external acting 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 and actuators used in optical and electrical memory switching, information storage and transform 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 direct covalent-linked neighbors (two-fold coordinated chalcogen atoms S, Se or Te);
- relatively large content of free volume frozen near glass transition as additional volume over ones proper to isocompositional extrapolated supercooled and thermodynamically equilibrium crystalline states;
- specific lone-pair character of electronic states of chalcogen atoms localized near top of a valence band as the 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 high-reliable AChS-based electronics. This time-instability effect 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 acting factors such as high-energy irradiation, thermal or absorbed light exposure, this process occurs too being known 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 [9]. In spite of complicity, the great number of models was proposed to explain the microstructural origin of these effects [8-10]. However, 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) [9, 11-15], 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 effects in AChS can be described as a system of externally-activated radiative and non-radiative disturbances followed by corresponding relaxation towards thermodynamic equilibrium.

In such a way, the known photoinduced phenomena in thin AChS films (both darkening and bleaching, scalar and vector, static and dynamic), their thermal and photo-induced erasing, etc. were simply explained in dependence on their chemical composition [11-15]. However, the CCM developed for this purpose did not take into account the accompanied processes of physical ageing proper to AChS, as well as 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 should be groundede on both native- and metastable-related states in AChS. Within this model, all kinds of known induced effects can be divided on two main groups – the under-irradiation or transient effects (*in-situ*) and post-irradiation ones (*ex-situ*). The latter is also known as post-irradiation physical ageing, they occurring at ambient (natural physical ageing) or thermal restoration conditions (thermally-induced physical ageing). The proposed CCM is shown in Fig. 1.

The first element of this model is associated with ground or initial structural state of AChS, representing itself as multiwell quasi-parabola (see Fig. 1). The deepest parabolic-like state within this quasi-parabola X corresponds to the most stable atomic equilibrium within glass-forming network. This state can be occupied by atoms in local configurations appeared during prolonged physical ageing under natural conditions. This process tending sometimes more than a few decades [16,17] occurs through long-term structural shrinkage of glassy backbone to eliminate additional free volume associated with its non-optimized under-constrained (floppy) 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 over-barrier tunneling [11]. The total number of ground-related parabolic wells is shown to be equal 3 for most AChS. In the normal conditions, the Z_1, Z_2,… sub-states are unstable, being characterized by relatively low energetic barrier close to ~kT.

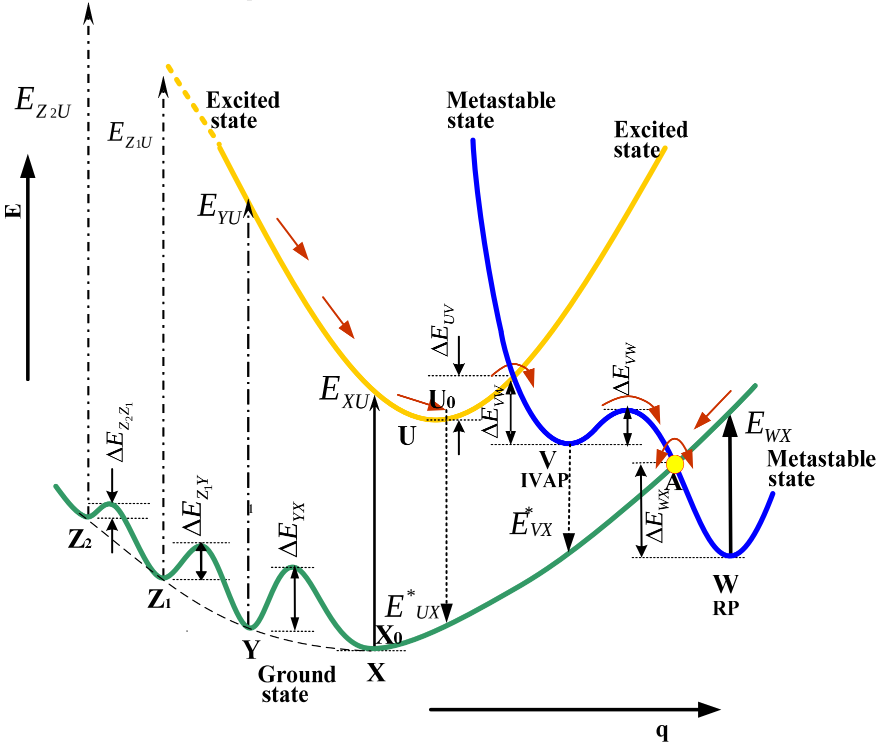

Fig. 1. Configuration-coordinate diagram describing complex externally-induced effects in AChS.

The overbarrier $Z_2 \rightarrow Z_1 \rightarrow Y$ transition corresponds to short-term physical ageing. This process occurs, in part, due to twisting of chalcogen atoms followed by twisting-related shrinkage of glassy network, while the over-barrier transition from Y into X state is associated with more prolonged (a so-called long-term) physical ageing [18].

The second element of the proposed energetic diagram (Fig. 1) corresponds to the excited sate U, 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 covalent-bonded AChS networks [5]. It should be noted this short-term state is always single-well, despite a variety of external influences applied to AChS. Only vertical radiation-induced Frank-Condon-type transitions with E_{XU}, E_{YU}, E_Z energies are possible between ground sub-states X, Y and Z and excited state U. The shortest among them E_{XU} corresponds to photo- and radiation-induced darkening, while E^*_{UX} transition (possible at low temperature) being responsible for photoluminescence excitation. Such effects are accompanied by structural relaxation of atomic centres with significant changes in their configurational coordinate q, the difference in E_{XU} and E^*_{UX} energies corresponding to Stocks shift [5].

The transition of $X \rightarrow U \Rightarrow U^0$ describes band-band excitation, while Z_2, Z_1, $Y \rightarrow U \Rightarrow U^0$ transition is related to alternative high-energy band-band excitation. In contrast, the backward $U^0 \rightarrow X \Rightarrow X^0$ transition corresponds to radiative recombination into a ground state. All these transitions followed by structural relaxation in a potential well.

The third element of the developed CCM is associated with metastable state (Fig. 1). This state can be presented by parabola, which splits into two quasi-parabola *W* and *V* in accordance to different types of defects created. The first quasi-parabola *W* corresponds to the closed coordination defect pairs known as IVAP (the intimate valence alternative pairs, conjugate pairs of charged defects), while the second quasi-parabola *V* corresponds to randomly distributed coordination defects like to VAP (the valence alternative pairs) [19]. Due to small energy barrier between excited and metastable states ΔE_{UV} at the normal conditions ($\sim kT$), the atomic centers relax from *U* state into *V*-*W* state via exciton self-trapping.

In general, the AChS can relax in the ground state *X* too due to irradiative E^*_{UX}, transition, but this transition is impossible at normal condition because of small ΔE_{VW} barrier. This is a reason for short lifetimes of atomic centers occupied *V* sub-state. All atomic centers finally relax through A point (Fig. 1) into *W* state with P_W^A probability (the first channel) or into ground state *X* with (1- P_W^A) probability (the second channel). The atomic centers in *W* state are quite stable, since their transition in the ground E_{WX} state is possible only due to additional thermal heating. In the result of such thermally-activated process, the A point will be multiply appeared in the path of atomic centers relaxation.

In full respect to the above CCM, we can put forward a set of differential equations describing balance of possible physical processes in AChS.

The rate equation of atomic sites in the ground state *X* can be presented as:

$$\frac{dN_X}{dt} = \frac{N_Y}{\tau_{YX}} - Q\sigma_X N_X + k_r^{UX} N_U + \frac{N_V\left(1 - P_W^A\right)}{\tau_{VW}\left(1 - Q\sigma_W\left(1 - P_W^A\right)\right)}, \quad (1)$$

where

N_X, N_Y, N_U, N_V denote the numbers of atomic sites in *X, Y, U* and *V* states, respectively,

Q – the excitation flux (photons, gamma-quanta, electrons, etc.),

σ_X, σ_W – the cross-sections of photon absorption from *X* and *W* states, respectively,

k_r^{UX} – the recombination rate for radiative transition from *U* into *X* state,

P_W^A – the splitting probability for relaxation fluxes between *X* and *W* states in the A point,

τ_{YX}, τ_{VW} – the lifetimes of atomic sites in *Y* and *V* states, respectively.

As has been shown earlier [9], the lifetimes of atomic centers in any metastable state was determined by thermal transition into more stable state over corresponding energetic barrier ΔE. Hence, the lifetime of atomic centers in *Y* state, τ_{YX}, which determines transitions into *X* state over the energetic barrier ΔE_{YX}, can be estimated as:

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

where

ν_{YX} is the "attempt" frequency (the order of the frequency of vibrations in the well).

In a similar manner, the lifetime of atomic centers in *V* state, which determines thermal transition into *W* state over the energetic barrier ΔE_{VW}, is equal to

$$\tau_{VW}^{-1} = \nu_{VW} \exp\left(-\frac{\Delta E_{VW}}{kT}\right), \quad (3)$$

where

ν_{VW} is the 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* and *W* ones, while the second term describes the capture of atomic centers from *X* into excited *U* state.

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

$$\frac{dN_Y}{dt} = \frac{N_{Z_1}}{\tau_{Z_1Y}} - Q\sigma_Y N_Y - \frac{N_Y}{\tau_{YX}}, \quad (4)$$

where

N_{Z_1} – the number of atomic sites in Z_1 state;

σ_Y – the cross-sections of photon absorption from *Y* state;

τ_{Z_1Y} – the lifetime of atomic sites in Z_1 state, determined analogously to (2) and (3).

The first term in Eq. (4) corresponds to relaxation of atomic centers from Z_1 into *Y* state, while the second and third ones – to capture of atomic centers into excited *U* and ground *X* states.

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

$$\frac{dN_{Z_1}}{dt} = \frac{N_{Z_2}}{\tau_{Z_2Z_1}} - Q\sigma_{Z_1} N_{Z_1} - \frac{N_{Z_1}}{\tau_{Z_1Y}}, \quad (5)$$

where

N_{Z_2} – the number of atomic sites in Z_2 state;

$\tau_{Z_1Z_2}$ – the lifetime of atomic sites in Z_2 state.

σ_{Z_1} – the cross-section of photon absorption from Z_1 state.

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 terms – 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:

$$\frac{dN_U}{dt} = Q\left(\sigma_x N_x + \sigma_Y N_Y + \sigma_{Z_1} N_{Z_1} + \sigma_{Z_2} N_{Z_2}\right) - k_r^{UX} N - \frac{N_U}{\tau_{UV}}, \quad (6)$$

where

τ_{UV} – the lifetime of atomic sites in *U* state;

σ_{Z_2} – the cross-section of photon absorption from Z_2 state.

The first term of Eq. (6) corresponds to capture of atomic centers into *U* state from all ground-related states (X, Y, Z_1, Z_2), while the second and third terms – to relaxation of atomic centers from *U* state into *X* and *V* ones, respectively.

Finally, the rate equation describing atomic sites in metastable *V* state can be given as:

$$\frac{dN_V}{dt} = \frac{N_U}{\tau_{UV}} - \frac{N_V}{\tau_{VW}} - k_r^{VX} N_V \,, \qquad (7)$$

where

τ_{VW} – the lifetime of atomic sites in *V* state;

k_r^{VX} – the rate of recombination from *V* into *X*. state.

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

Taking into account that:

$$\frac{N_V}{\tau_{VW}} = \begin{cases} X \to \left(1 - P_W^A\right) \\ W \to P_W^A \end{cases}, \qquad (8)$$

the rate equation describing atomic sites in metastable *W* state is

$$\frac{dN_W}{dt} = \frac{N_V}{\tau_{VW}} P_W^A - \sigma_W Q N_W + \frac{N_V P_V^A}{\tau_{VW}\left(1 - \sigma_W Q P_W^A\right)}, \qquad (9)$$

where

N_W is the number of molecular fragments in *W* state;

σ_W is the cross-section of photon absorption from *W* state.

It should be noted that the first and third terms in Eq. (9) correspond to relaxation of atomic centers from *V* state, while the second term – to capture of atomic centers from *W* state.

3. Conclusions

The universal configuration-coordinate model described induced structural transformations in amorphous chalcogenide semiconductors was developed. The proposed model can be used to adequately describe the known induced phenomena such as:

- time instability during glasses conservation in normal conditions before and after irradiation;
- dose dependences of radiation-induced optical changes, caused by corresponding coordination defects formation;
- thermal relaxation caused by additional temperature treatment of the irradiated glasses;
- complicated effects owing to simultaneous multifactor external influences (photo-thermally-induced, radiation-thermally-induced, photo-radiation-induced, etc.).

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