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RELAXATION-DEGRADATION PHOTOINDUCED KINETIC EFFECTS IN THIN CHALCOGENIDE FILMS

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Photoinduced effects in thin chalcogenide films are known to be a ground for their multifunctional application in optoelectronic information systems as well as in a wide range of post-technological optimization routes. Nevertheless, the kinetics of these effects is relatively poorly studied up to now.

This work is aimed to search adequate functional expressions suitable for kinetics of photoinduced optical effects in As₂S₃ thin films, taking into account the main principles of previously developed approach to similar phenomena in topologically-disordered solids.

Key words: photo-induced effects, metastable state, potential well, relaxation function.

Amorphous chalcogenide semiconductors (AChS) have been studied intensively, because these materials exhibit a number of interesting induced effects in their structure, paramagnetic, electronic and optical properties giving a ground for various electronics switching and memory devices, sensing and imaging applications, etc. [1, 2]. These effects are supposed to be owing to (1) high flexibility of glass matrix with atoms of low atomic coordinations, (2) relatively large content of free volume frozen near glass transition and (3) specific lone-pair character of electronic states localized near the top of valence band [3].

At the same time, the number of negative relaxation-related effects can be observed during AChS application, especially time instability in their physical properties connected with decay of metastable post-technological structure caused by external factors. The obvious reason for this relaxation is tending towards more equilibrium state (even in the normal conditions at so-called natural physical ageing) proper to metastable solids like to AChS. The presence of time-dependent relaxation processes causes some complications in the phenomenological description of induced phenomena in AChS.

Up to now, only single separate effects of external influences were explained well in AChS, in particular, the recombination of non-equilibrium carriers [4], photodarkening [5–8], photocurrent increase [7] etc. Nevertheless, the proposed models

do not pretend on universality, since they describe only one certain type of processes without consideration of all peculiarities of concomitant relaxation.

In this paper, the principally alternative model for description of complex effects of externally induced influence in AChS will be examined.

Within this model, we divide all kinds of known induced effects on two main groups – the under-irradiation or transient effects (*in-situ*) and post-irradiation or physical ageing ones (*ex-situ*), the latter being post-irradiation at ambient conditions (natural physical ageing) and post-irradiation at thermal-restoration conditions (thermally-induced physical ageing).

Let's accept in full agreement with general energetic approach describing AChS structure [3–6] that all possible states are characterized by energy E connected with some geometric figures like to parabola or its different modifications – bi-, tri-, tetra- or multi-parabola (in dependence on AChS specifics) with character generalized configuration coordinate q (see fig. 1).

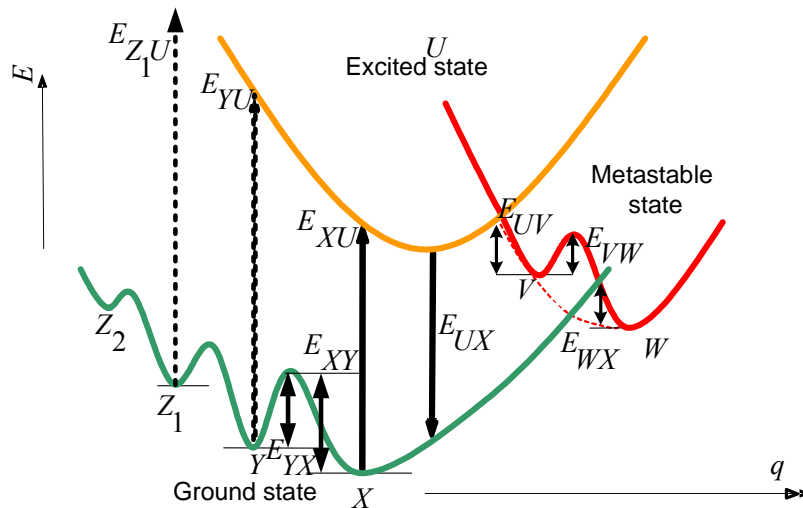


Fig. 1. Configuration-coordinate diagram describing complex externally-induced effects in AChS

As it testified from fig. 1, the first element of configuration-coordinate model (the ground or initial state) represents itself as multi-well quasi-parabola, the deepest parabolic state X corresponding to most stable atomic equilibrium within glass-forming network. This state can be satisfied owing to prolonged physical ageing of AChS under natural conditions. Other ground states Y , Z_1 , Z_2 , ... are characterized by more shallow potential wells, the inter-well transitions between them being thermally activated. It is supposed that kinetics of these transitions are described by over-barrier tunneling like to atomic twisting [6]. The total number of ground-related parabolic wells is shown to be equal 3 for most kinds of AChS. In the normal conditions, the Z_1 , Z_2 , ... sub-states are

unstable, being characterized relatively by low energetic barrier $\sim kT$. The over-barrier $Z_2 \rightarrow Z_1 \rightarrow Y$ transition corresponds to short-term physical ageing, while transition over barrier from Y into X state is associated with long-term physical ageing [9, 10].

The second element U (the excited state) can be presented by single parabola with wide-stretched edges in accordance to strong electron-phonon coupling proper to covalent-bonded AChS networks [3]. This state is single-well, despite a variety of external influences, which can be applied to the glass system. Only vertical radiation-induced Frank-Condon-type transitions follow by significant configurational disturbances are possible between initial and excited states.

The third element of configuration-coordination diagram is the parabolic-like too, it corresponding to long-term metastable states related with essential reconstruction of glass structure. This state can be presented by parabola, which split to two quasi-parabola W and V in accordance to different types of defects created. The first quasi-parabola W corresponds to closed coordination defect pairs known as IVAP (the intimate valence alternative pairs), while the second quasi-parabola V corresponds to randomly distributed coordination defects like to VAP (the valence alternative pairs) [3].

As can see from Fig.1, the metastable state has the common point of crossing between excited and initial ground parabolas. Due to small potential barrier between excited and metastable states ($\Delta E_{UV} \sim kT$) the glass matrix can relax from excited state U in both V and W metastable states. It should be noted that the corresponding lifetimes for atomic centers in V sub-state is extremely small and all atomic centers transform finally from this state into W sub-state. In the case of small energetic barrier ΔE_{WX} ($\Delta E_{WX} < kT$), all defects in W sub-state annihilate in the ground state X . If $\Delta E_{WX} > kT$, the stable defects in W sub-state appear (they can annihilate into the ground state only after additional thermal treatment).

In the present paper, we shall focus our study on photo-induced relaxation in As_2S_3 thin films in the term of the above configuration-coordinate model.

The studied As_2S_3 thin films were prepared by thermal evaporation in a vacuum on glass substrate, their thickness being in the range of 1,0–1,3 μm . These thin films were illuminated by He-Ne laser beam ($\lambda=633$ nm) with power density of 110 mW/cm², the optical transmission spectra in the region of fundamental optical absorption edge being chosen as control parameter. Under these conditions (marked for simplicity as the regime 1), the accompanied thermal annealing of the illuminated thin films is supposed to be the most significant.

For comparison, we used also results of illumination for As_2S_3 films obtained by other authors [11, 12]. They differ mainly by accompanied thermal heating of the studied films. Thus, in [11] (the regime 2), the As_2S_3 films were photoexposed by halogen lamp equipped with IR-cut filter at 50 mW/cm² incident power density, the optical band gap Eg being chosen as control parameter. In [12] (the regime 3), the studied As_2S_3 films were photoexposed by Ar-laser beam ($\lambda=633$ nm) with 15,6 mW/cm² power density, the diffraction efficiency being chosen as control parameter. Hence effect of uncontrolled thermal heating enhanced within regimes row 3–2–1.

Since the shape of relaxation curves in all above regimes revealed the character non-monotonous shape, the simulation of corresponding kinetics were carried out by sum of different relaxation functions (RF), as it was first proposed in [13, 14]. The following combinations of RF were tested, in part:

- the both RF are exponential ones (ERF);
- the both RF are bimolecular ones (BRF);
- the both RF are stretched-exponential ones (SERF);
- the first RF is exponential and the second RF is stretched-exponential;
- the first RF is exponential and the second RF is bimolecular;
- the first RF is stretched-exponential and the second RF is bimolecular.

With a purpose of adequate mathematical description of the observed relaxation kinetics, the numerical values of fitting parameters of the above RF combinations were calculated in such a way to minimize the mean-square deviation *err* of the experimentally measured points from the chosen sum of RF sum [13, 14]. The most suitable sum, describing the observed process, was chosen at the basis of comparison of the calculated *err* values. The developed PC-program package permits us to establish unambiguously, on the basis of the obtained experimental data, the type of RF sum describing photoinduced relaxation and, consequently, to assume their mechanism in the term of known configuration-coordinate model.

The results of mathematical simulation are presented in table 1.

Table 1

Mean-square deviations (*err*) for different sum of RF describing photoinduced relaxation in thin As₂S₃ films

RF	Values of <i>err</i>		
	regime 1	regime 2	regime 3
EFR+ERF	$20 \cdot 10^{-6}$	$27 \cdot 10^{-8}$	$2.96 \cdot 10^{-2}$
BFR+BRF	$20 \cdot 10^{-6}$	$160 \cdot 10^{-8}$	$7.22 \cdot 10^{-2}$
SERF+SERF	$2.2 \cdot 10^{-6}$	$71 \cdot 10^{-8}$	$1.85 \cdot 10^{-2}$
ERF+SERF	$5.7 \cdot 10^{-6}$	$8.2 \cdot 10^{-8}$	$2.29 \cdot 10^{-2}$
ERF+BRF	$10 \cdot 10^{-6}$	$260 \cdot 10^{-8}$	$1.73 \cdot 10^{-2}$
SERF+BRF	$20 \cdot 10^{-6}$	$350 \cdot 10^{-8}$	$6.04 \cdot 10^{-2}$

As it testified from table 1, the ERF is proper for all photoinduced kinetics in the studied films whichever the corresponding regime of their illumination. This result can be explained due to preference of *in-situ* photoinduced activation in the total balance of processes occurred (complex photo and thermoinduced relaxation). Within configuration-coordinate diagram (see fig. 1), this photoinduced *in-situ* process corresponds to transition of carries from ground into excited state ($X, Y, Z \rightarrow U \rightarrow V$ transition on fig. 1). Under increasing temperature (as a result of film heating), the kinetics of photoinduced *in situ* process tends to stretched-exponential behavior SERF with non-exponentiality index (power index) more than 1, which corresponds to threshold tendency.

Simultaneously, the process of annihilation of coordination defects (or, alternatively, pairs of under- and over-coordinative atoms) takes place, its kinetics describing by BRF [13]. This process corresponds to $V \rightarrow X$ or $V \rightarrow W$ transitions on configuration-coordinate diagram (fig. 1). Increase in the temperature leads to stretched-exponential kinetics too with power index more than 1 owing to thermally-activated dispersivity additionally to initial atomic-structural dispersivity (transition $W \rightarrow X$ on configuration-coordinate diagram).

The known photoinduced optical effects in As_2S_3 thin films reveal complex kinetics associated with pure activation-type *in-situ* photoexcitation with simultaneous backward structural transformations due to uncontrolled thermal heating. This kinetics can be adequately described by sum of two relaxation functions proper to each elementary component, the exponential-like behavior being dominant in the main photoinduced process whichever photoexposure conditions.

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**КІНЕТИКА РЕЛАКСАЦІЙНО-ДЕГРАДАЦІЙНИХ
ФОТОІНДУКОВАНИХ ЕФЕКТІВ
У ХАЛЬКОГЕНІДНИХ ТОНКИХ ПЛІВКАХ**

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Як відомо, застосування халькогенідних плівок в інформаційних системах оптоелектроніки та широкі можливості їх пост-технологічної оптимізації базуються насамперед на відомих фотоіндукованих ефектах. Проте кінетика цих ефектів на сьогодні вивчена недостатньо.

Метою статті є відшукати функціональний вираз для опису кінетики фотоіндукованих ефектів в тонких плівках As_2S_3 , беручи до уваги основні принципи попередньо запропонованого підходу до опису подібних явищ в топологічно-розпорядкованих твердих тілах.

Ключові слова: фотоіндуковані ефекти, метастабільний стан, потенціальна яма, релаксаційна функція.

**КИНЕТИКА РЕЛАКСАЦИОННО-ДЕГРАДАЦИОННЫХ
ФОТОИНДУЦИРУЕМЫХ ЭФФЕКТОВ
В ХАЛЬКОГЕНИДНЫХ ТОНКИХ ПЛЕНКАХ**

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Как известно, применение халькогенидных пленок в информационных системах оптоэлектроники и широкие возможности их пост-технологической оптимизации базируются в первую очередь на известных фотоиндуцируемых эффектах. Однако кинетика этих эффектов на сегодня изучена недостаточно.

Целью статьи является отыскание функционального выражения для описания кинетики фотоиндуцируемых эффектов в тонких пленках As_2S_3 , принимая во внимание основные принципы предварительно предложенного подхода к описанию подобных явлений в топологически-упорядоченных твердых телах.

Ключевые слова: фотоиндуцируемые эффекты, метастабильное состояние, потенциальная яма, релаксационная функция.

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