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ABSTRACT BOOK

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STRUCTURAL DISORDERING IN CHALCOGENIDE GLASSY SEMICONDUCTORS: CRITICAL ASSESSMENT ON SPECULATIONS WITH RADIATION-INDUCED METASTABILITY

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Effects of radiation-induced metastability have been well justified in chalcogenide glassy semiconductors (ChGS) since the earliest 1960-s, the time of extensive research just after pioneering invention of ChGS' semiconductor properties by N.A. Goryunova and B.T. Kolomiets. Microstructure mechanism of radiation-induced effects (RIE) has been scrupulously studied nearly three decades ago (see, for example, ref. [1] and literature therein). Now it is commonly accepted that destruction-polymerization transformations (DPT) are responsible for RIE. These DPT occur as destruction of one covalent bond followed by formation of new one, they being considered as an elementary precursor of new metastable state, having two atoms of glassy network in an abnormal coordination not obeying the Mott's *8-N* coordination rule [1-3]. These atoms, the over- and under-coordinated ones, create diamagnetic pair of charged defects, because, in addition to "wrong" coordination, they have opposite electrical charges. Alternatively, this process can proceed as non-defect transformation, provided two covalent bonds are re-switched simultaneously. Under ambient irradiation conditions (in unprotected environment), these DPT lead to own (intrinsic) and impurity (extrinsic) transformations.

Nevertheless, recently some authors [4-7] employing a number of erroneous data tried to reconsider this model in favor of speculative approach combining defect and non-defect origin for RIE in dependence on ChGS composition. Ignoring essential difference between photo- and radiation-induced phenomena, they ascribed identical explanation for structural metastability in both bulk glass and thin-film ChGS probes. Main sources of these misunderstandings are related to (1) unproved pre-history of glassy samples under microstructure research (without information on strict ChGS composition, thermal and irradiation treatments, etc.), (2) invalid methodological protocols for ex-situ research (cycles of microstructure measurements are essentially separated in time and even in space after irradiation), (3) speculations with under-margin "radiation-induced" changes, which are far below *percolation level* for ChGS (the *systematic error* bar for ex-situ arranged measurements are replaced by *fitting errors* of mathematical treatment programs), (5, what is the most important) full absence of direct signatures of principal RIE (optical measurements are ignored at all, or performed, in the best case, too late after irradiation finishing, sometimes more than ten years), etc.

In this report, we give critical assessment of such speculations, disclosing their misleading character and inconsistence with basic principles of Glass Physics.

Our argumentation is supported by results of complex, comprehensive and systematic research performed on γ-irradiated, annealed and rejuvenated bulk As_xS_{100-x} glasses using positron annihilation technique (positron lifetime measurements and Doppler broadening of annihilation radiation) in a *backward measurement chronology* [8-10]. It is demonstrated that RIE in positron trapping modes of ChGS are in strict correlation with shift of their optical absorption edge. The competitive processes of free-volume void evolution such as *agglomeration-fragmentation*, *expansion-contraction* and *charging-discharging* are considered as possible stages of radiation- and thermally-induced structural transformations. Meaningful model for RIE and relaxation-driven evolution in As-S glasses is proposed. So analysis of different void evolution processes in ChGS under external influences allows establish correlation of observed changes in positron trapping modes with real structural transformations. Thus, free-volume evolution in As_xS_{100-x} glasses associated with thermally- and γ-induced aging is associated with void *fragmentation*, while γ-induced defect formation leads mainly to void *charging*. Finally, the configuration-coordinate model describing phenomenological features of radiation-and-thermally-induced metastability in ChGS is developed [1,11].

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