

Photoinduced conversion between lone-pair and bonding electrons in S enriched Ge–S glasses

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A bond-conversion model is proposed to explain the photoinduced structural changes in chalcogenide glasses. An essential role in this model is played by lone-pair electrons of chalcogen atoms which are converted into bonding ones under photoexcitation causing the structure building.

Предложена модель конверсии химической связи для объяснения фотоструктурных изменений в халькогенидных стеклах. Основная роль в этой модели принадлежит уединенным электронам атомов халькогена, которые при фотовозбуждении преобразуются в связывающие, приводя к перестройке структуры.

Chalcogenide semiconductors are very promising materials for optical and optoelectronic devices such as image sensors and non-volatile memories. To understand the mechanism of reversible photoinduced structural changes in those materials, the Raman spectra study is often used offering the information on local bonds in the material.

In this paper, we consider our previous experimental results on the Raman spectra study of non-stoichiometric $\text{Ge}_{20}\text{S}_{80}$ glassy semiconductors [1] and propose a bond conversion model which can explain the photoinduced structural changes.

A non-stoichiometric Ge–S glass is believed generally to be built up by tetrahedral GeS_4 units with extra S atoms incorporated in the chains linking the tetrahedral molecules. With increasing S content, the number of S–S units grows, resulting in large atomic clusters of S. Although the germanium chalcogenides have been intensively studied during the last fifteen years, the knowledge of the clusters of S in S enriched glasses is still ambiguous. Such clusters can consist of the two allotropic forms, which are mixed together: one is the helical chain while the other is formed by small ring-like groups of S atoms and randomly oriented in chalcogenide glasses.

We have shown in our Raman spectra study [1] that the photoinduced changes take place only in the S-chain vibrations and manifest themselves as an increase in the Raman vibration frequency. If the sample is re-excited again after the irradiation was interrupted for several hours, its Raman spectrum returns to the original state although with some distinctions. To explain the obtained results, we propose a bond-conversion model for photoinduced structural changes, according to that model, the bonding configurations are rearranged due to new covalent bond formation, as shown in the Fig.1. Since in S-rich Ge–S films extra S atoms are incorporated in the chains, for the simplicity in the Fig.1, a, the structure is illustrated as parts of S chains. An essential role in this model is played by lone-pair (LP) electrons of chalcogen atoms which define the top of valence band [2]. It is reasonable to assume that the band-band irradiation excites one of LP electrons of chalcogen atom to the conduction band. So chalcogen atoms have now unpaired electrons on the former LP orbitals. As a result of the electron excitation, the molecular interaction between neighboring S atoms from different chains changes from the Van-der-Waals one to the stronger