

DOH 04 OPTICAL MONITORING OF SOLID ELECTROLYTES FORMATION IN QUATERNARY ALLOYS Ag: AsS₃-GeS₄ AND THEIR ANALYSIS

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Quaternary solid electrolytes based on Ag photodoped glasses (GeS₄)_x(AsS₃)_{1-x} (0 ≤ x ≤ 1) have been fabricated and studied. The process of fabrication consists of: the synthesis of glassy materials followed by their structural and electrical characterization; preparation of thin films and deposition of Ag layers; realization of a controlled Ag photodissolution (PD) processes that results in formation of solid electrolytes. The chalcogenide glassy (ChG) backbones were prepared by melt-quenching method in vacuum from pure (99, 99%) As, S and Ge but the structure have been studied by XRD and far IR spectroscopy. The thin films have been prepared by thermal evaporation in vacuum of synthesized materials, onto Pyrex glass substrates. The thickness of the films was around 1 μm and the area of deposition being about 1,5 cm². The silver layers, with thickness of about 60 nm, were deposited on top of the ChG films, using the same method.

Fabrication of solid electrolytes was performed at room temperature, by PD of silver onto ChG films, using the light of a halogen 100W lamp focused by a quartz lens. The exposure was performed from the side of transparent substrate, but the power incident at the sample surface was estimated as ~ 250 mW/cm². The PD rate was measured by monitoring the changes that occur in the transmittance of the sample of weakly absorbed in ChG broadband light (λ = 650 - 3000 nm) cut by a filter KC-15 placed behind the sample, as described in [1, 2]. The obtained results have shown that the process of solid electrolyte formation occurs in three steps, but the last two steps, as well as the electrical properties of the finally fabricated electrolyte, is strongly influenced by chemical composition and microstructure of the used ChG backbone. The rate of light – induced solid state reaction between Ag and glassy (GeS₄)_x(AsS₃)_{1-x} films increases to a maximum around composition (GeS₄)_{0.33}(AsS₃)_{0.67} and then falls down. The maximum and minimum rate of reaction for different compositions differs by 20 times. On the other hand, the resistivity of the final obtained solid electrolytes decreases with GeS₄ increase, reaching a minimum around the same ChG composition. The appearance of a compositional maximum is probably due to macroscopic phase separation, which occurs by Ag photodissolution in chalcogen rich glasses [3]. The replacement of As atoms by Ge atoms in glassy (GeS₄)_x(AsS₃)_{1-x} leads to an increase in the concentration of tetrahedral [GeS]_{4/2} structural units (s.u.) and decrease of concentration of the trigonal [AsS]_{3/2} ones, maintaining the concentration of [S-S]_{2/2} s.u. nearly constant [2]. This is supported by IR transmission spectra. For AsS₃, this spectrum comprises only one main oscillation mode at 310 cm⁻¹, characteristic for As–S bond. Introduction of about 7 at.% Ge, that is alloy (GeS₄)_{0.33}(AsS₃)_{0.67}, results in appearance of an additional oscillation mode, at 374 cm⁻¹, characteristic for Ge –S bond. We assume that the above mentioned peculiarities of solid electrolyte formation and its low resistivity for composition (GeS₄)_{0.33}(AsS₃)_{0.67} may be due to its homogenization due to building of an amalgamation of tetrahedral and trigonal structural units connected in a random network, without clustering. Such homogenization promotes the transport of both electrons and ions involved in photoreaction [4] because of lack of phase boundaries and additional defects. Thus, the quaternary solid electrolyte Ag: (GeS₄)_{0.33}(AsS₃)_{0.67} seems to be the best between studied ones for further applications.

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