

Light-induced bleaching and refractive index change in vitreous AsS₃-GeS₄ thin films

M. Ciobanu¹, A-C. Galca², A. Velea², E. Stoianova¹, A. Afanasiev¹, D. Tsiulyanu^{1*}

¹Technical University of Moldova, Blvd Dacia 41, Chisinau, MD-2060, Republic of Moldova

²National Institute of Materials Physics, Atomistilor 405A, 077125 Magurele, Romania

***Email:** tsiudima@gmail.com

Abstract: Light-induced structural transformations (LIST) in chalcogenide glasses (ChG), discovered about 50 years ago, still remain a unique phenomenon, very large applied but not fully understood. The LIST results in variation of the optical and other properties of ChG when illuminated, which are called either photobleaching (PB) or photodarkening (PD) if the sample optical transmission at a specific wavelength increases or decreases respectively. To date, unambiguity is established that the optical effects at LIST (especially in thin films) are largely associated with glass composition, technology of preparation and post preparation thermal treatment. The present paper is conducted to investigate photoinduced effects in vitreous thin films of the pseudo - binary system AsS₃ - GeS₄, which belong to an intermediate topological phase. Some compositions from these glasses exhibit the advanced degree of structural self-organization (SSO) [1], so we could track whether the SSO influences the photoinduced effects. The AsS₃ - GeS₄ thin films have been prepared via thermal vacuum evaporation of the beforehand synthesized counterpart glassy alloys, onto quartz substrates. We studied the spectral distribution of both optical absorption (α) and refractive index (n) of the films, before and after their exposing to an integral light with $h\nu > E_g$ and irradiance 39 mW/cm². Measurements were performed in the 350 – 1770 nm spectral range, using the Spectroscopic ellipsometry method. To exclude the thermal irreversible phenomena, before measurements all samples have been annealed at 149 °C / 24 h. It was found that exposure to light of the examined glasses leads to their photobleaching, with the exception of GeS₄, which darkens slightly. The level of PB strongly depends on the glass composition and spectral range of the probing light. The largest PB has been observed in Ge free films (AsS₃), as well as in films of ternary As_{11.1}Ge_{11.1}S_{77.8}, which are known as films with a large degree of SSO [2]. The refractive index (n) follows the usual curves of a normal dispersion, for all samples of AsS₃-GeS₄, materials measured before and after illuminating experiments. It gradually decreases along entirely used spectrum range, as the content of GeS₄ increases, so that the n of Ge free glass (AsS₃) exhibits the highest value, separately among unexposed and exposed samples. Light exposing differently affects the refractive index of films based on the ChG in question, so that in AsS₃, it slightly increases while when the composition of the film changes from Ge-deficient to rich, it imposingly decreases. Thus, an interesting crossover of Δn from positive to negative values occurs, which points to different mechanisms of LIST in germanium-enriched glasses and arsenic enriched one.

Keywords: Chalcogenide glasses, thin films, AsS₃-GeS₄, photoinduced phenomena.

References

1. D. Tsiulyanu, M. Veres, R. Holomb, M. Ciobanu, Raman scattering evidence on the correlation of middle range order and structural self-organization of As-S-Ge glasses in the intermediate phase region, J. Non-Cryst. Solids, 609, (2023)122255 (1-10). <https://doi.org/10.1016/j.jnoncrsol.2023.122255>
2. M. Ciobanu, A.C. Galca, F. Sava, M.Y. Zaki, A. Velea, D. Tsiulyanu, First Sharp Diffraction Peak features of the intermediate phase glasses and amorphous thin films in the non-toichiometric (GeS₄)_x(AsS₃)_{1-x} system, Thin Solid Films, 773 (2023) 139828 (1-8). <https://doi.org/10.1016/j.tsf.2023.139828>

Acknowledgement:

This work was supported by Ministry of Education and Research of the Republic of Moldova; Institutional subprogram **021201**