New Functional Materials Based on Chalcogenide Glasses, Polymers Obtained Via Modification and Nanocomposite Techniques and Their Applications

Stronski A.[1], Achimova E.[2]

[1] *V. Lashkaryov Institute of Semiconductor Physics NAS of Ukraine, Kyiv, Ukraine*
E-mail: paiuk@ua.fm
[2] *Institute of Applied Physics AS of Moldova, Chisinau, Moldova*

In this work design and synthesis of new nanocomposite materials based on chalcogenide glass semiconductors (ChGS), organic polymers, together with overview of their properties and some applications are reviewed.

Influence of doping of chalcogenide glasses by transitional metals and rare-earth elements on their properties is considered. X-ray diffraction measurements confirmed the amorphous structures of chalcogenide glasses doped by transition metals and rare-earth elements. Radial distribution functions have not shown significant changes in distance for nearest neighborhood with the change of dopant concentration. Differential scanning calorimetry (DSC) measurements have shown that T_g values were smaller for doped glasses as compared to undoped ones. Activation energy of glass transition was estimated with the use of Kissinger's expression. The main feature of Raman spectra under the introduction of transitional and rare-earth impurities into chalcogenide glass matrix is change of relative concentration of the main and non-stoichiometric structural elements typical for initial glasses. Luminescence of chalcogenide glasses doped by transitional metals was studied in 800-1600nm region (T=77K, $\lambda_{ex} = 514nm$). Photoluminescence appears as a broad Gaussian-shaped spectrum with peak energy E_{PL} approximately at $E_{PL} \approx E_g/2$. Chalcogenide glasses modified by Yb have two bands of luminescence in near IR region (near 980 and 1060nm) with excitation on 980nm wavelength at room temperature. In this case transitions observed are characteristic for Yb^{3+} ion. Pure chalcogenide glasses are diamagnetics. Introduction of transitional and rare earth impurities changes the magnetic properties of investigated chalcogenide glasses. In the fields near 5T the specific magnetic moment M(T) dependence was observed which is characteristic for paramagnetic and ferromagnetic in the paramagnetic temperature range.

Two-component nanocomposites based on ChGS and metal phtalocyanine were obtained by simultaneous condensation of two components on the surface of substrates in a vacuum. Surface morphology of the samples was investigated using AFM. In the optical absorption spectra of composites the characteristic bands of phtalocyanine are present. Comparison of Raman spectra for nanocomposite films with ChGS and Me-ChGS allows identifying main structural bounds. Metal atom can form additional coordination bonds with chalcogen of nearby ChGS matrix.

Layers of polyepoxypropilcarbazole were studied as media for holographic recording. The polymer was synthesized as the host polymer matrix, and iodoform CHI_3 was introduced as the photosensitizing dye. As the pure polymer material is sensitive in the UV spectral range its sensitivity should be shifted to the type of recording laser region. To shift the spectral sensitivity to the blue spectral region the sensitizing dye such as iodoform CHI_3 has been doped into the polymer matrix. Thin polymer films with thickness ~ 1.3 μm were prepared from homogeneous polymer solution in toluene by spin-coating procedure using programmable spin-coater “SGS Spincoat G3P-8”. To determine the film thickness in this work the MII-4 interference microscope modified by developed interferometric software OPTIC METER and AFM measurements were applied. For holographic gratings recording 473 nm 100 mW DPSS laser was used. Diffraction gratings were recorded using these films as registering media by keeping the beams ratio 1:1 and spatial frequency 1000 lines/mm. After exposure of films by interference pattern the wet chemical treatment was applied for the surface relief formation. The etching was controlled by measuring the diffraction efficiency of the gratings in transmission mode at the 633 nm wavelength within the equal time intervals. Evolution of diffraction efficiency of the gratings in dependence on recording and etching times was studied. Diffraction efficiency values of obtained gratings were about 18%.

Nanomultilayer structures based on ChGS were studied as one-step recording media. Optical constants of nanomultilayers, thickness and optical band-gap energy were obtained from transmission spectra by Swanepoel method. Optical properties of nanomultilayer structures were analyzed within the frames of single-oscillator model. Diffraction gratings were recorded using DPSS green laser (λ=532nm and power 100mW) with synchronous diffraction efficiency measurement at λ=650 nm in the first diffraction order. AFM studies of surface relief of holographic gratings with a period Λ =1 μm recorded in nanomultilayers As_2S_3 –Se and $Ge_5As_{37}S_{58}$–Se have shown high optical quality of the obtained relief. Diffraction efficiency η values of the gratings were ~ 20-30% in transmission mode at wavelength λ = 0.65 μm. Due to the changes in transmission, reflection, and in thickness under the influence of laser irradiation, As_2S_3–Se and $Ge_5As_{37}S_{58}$ –Se multilayers may be used for effective amplitude-phase optical information media and surface-relief optical elements.

Different surface relief patterns were recorded by e-beam irradiation of nanomultilayer structures on the base of ChGS. Diffraction gratings with 1, 2 and 4 μm period and other surface relief’s structures were recorded by e-beam exposure using scanning-electron microscope Tesla BS 300 with programmable exposure control unit. The accelerating voltage was 25 kV and the size of the electron beam at this voltage was about 300 nm.

Obtained results show that optical, thermal, luminescent and magnetic properties of chalcogenide glasses can be changed by doping them with transitional and rare-earth metals. Chalcogenide glasses can be host for rare-earth metals which provide possibility to simultaneously change both luminescent and magnetic properties of glasses. Nanomultilayer composites based on chalcogenide glasses and inorganic (chalcogenide glass) - organic (polymers, dyes) composites are perspective as recording media. Direct surface recording or recording with consequent selective etching can be realized. New functional materials based on chalcogenide glasses, polymers and produced via modification and nanocomposite techniques are perspective for the applications in optics, optoelectronics and integrated optics.

The research was supported by the project FP–7 SECURE–R21

Dedicated to the 50-th anniversary of the discovery of light-sensitivity effect of thin films of chalcogenide glasses: M. T. Kostishin, E. V. Mikhailovskaya, P. F. Romanenko, G. A. Sandul, Journ. of Applied and Scientific Photography and Cinematography (in Russian), **10** (6), (1965) 450.