Preparation of non-uniform gradient structures on the basis of $Ge_{40}S_{60}$ alloys with modifiers

V.Yu.Loya, A.V.Lada *, S.S.Krafchyk, P.P.Puga, H.D.Puga*

Institute of Electron Physics, National Academy of Sciences of Ukraine,
21 Universitetska St., 88017 Uzhgorod, Ukraine

A comprehensive thermographic study of $Ge_{40}S_{60}$ combinations with modifiers (Pb, Al, Bi and Te) has been carried out. It has been shown that under heating, the modifier interacts with the $Ge_{40}S_{60}$ alloy occurs forming new compounds, i.e. $Ge_{40}S_{60}$-modifier ones. The technological conditions of the production of non-uniform gradient thin-film structures have been developed and the transmission and reflection spectra of those structures have been investigated. The dispersion of the refractive indices of thin-film gradient structures in the transparency region has been studied.

Проведены термографические комплексные исследования системы $Ge_{40}S_{60}$ с модификаторами (Pb, Al, Bi и Te). Показано, что при нагревании происходит взаимодействие модификаторов и сплава $Ge_{40}S_{60}$ с образованием новых соединений $Ge_{40}S_{60}$-модификаторы. Разработаны технологические условия получения неоднородных градиентных тонкопленочных структур, исследованы их спектры пропускания и отражения. В области прозрачности исследована дисперсия показателей преломления полученных тонкопленочных градиентных структур.

Introduction of modifiers into germanium chalcogenides influences considerably the optical and electro-physical properties of thin-film gradient structures based on the above materials [1]. Therefore, the search for modifiers affecting efficiently the physical properties of chalogenide materials, the investigations in interaction between the chalcogenide material (matrix) and modifier, in the influence of different nature modifiers and their concentrations on the properties of chalcogenide materials, and in production of thin-film gradient structures on their basis remain topical.

The vitrification region in the binary Ge–S system depends on the composition and when the latter approaches the GeS_2 and GeS ones, the vitrification possibility is limited [2]. In addition, the vitrification region in the Ge–S system depends considerably on the melt cooling regime, and the hardness of tempering conditions defines not only location of the vitrification region boundaries, but also the general possibility of glass production. Only the use of the hard tempering methods provides obtaining the GeS_2, GeS alloys in the vitreous state. The $Ge_{40}S_{60}$ alloy was chosen for studies, being, according to the phase diagram [2], at the crystalline/vitreous phase boundary. It has been predicted that the use of the $Ge_{40}S_{60}$ alloy, depending of the conditions of synthesis, alloy thermal treatment, introduction of different nature modifiers, their concentration, and technological conditions of the thin-film gradient structure preparation, will provide the alloy of different phase composition to be prepared.

In this work, the possibility of interaction between the matrix ($Ge_{40}S_{60}$ alloy) and modifiers of various nature (i.e. bismuth, lead, tellurium, and aluminum), their influence on the technological conditions of preparation and on the properties of non-uniform gradient structures have been studied. The $Ge_{40}S_{60}$ alloy was synthesized in quartz ampoules evacuated down to $1.5 \cdot 10^{-3}$ Pa residual pressure by fusing the calculated

quantities of germanium and sulfur. The $Ge_{40}S_{60}$ alloy melt was cooled down in air and in cold water with electric oven being turned off. To study the possible interaction between the matrix and modifiers, thermographic studies of the $Ge_{40}S_{60}$ alloy mixed with the modifiers using a Paulik-Erdey-Paulik derivatograph were carried out in three modes: initial heating from room temperature up to 1273 K at 5 deg/min heating rate, cooling at 3–8 deg/min rate and the repeated heating at 5 deg/min rate from room temperature up to 1273 K. These studies have shown that within the 633–793 K range, the matrix ($Ge_{40}S_{60}$ alloy) and modifiers (bismuth, lead, tellurium and aluminum) interact with formation of ternary compounds ($Ge_{40}S_{60}$-modifiers). This is evidenced by the presence of one or more exothermic interaction effects and two endothermic effects of melting ($Ge_{40}S_{60}$ alloy and $Ge_{40}S_{60}$-modifier ternary compound) in the above temperature range. Table 1 lists crystallization, melting and interaction temperatures for the $Ge_{40}S_{60}$-modifier system.

We have studied the influence of various modifiers on the technological conditions of production and on the properties of non-uniform thin-film $Ge_{40}S_{60}$ alloy-based gradient structures. A modified Vekshynsky

method (thermal evaporation in $3{\cdot}10^{-4}$ Pa vacuum) with two independent eccentrically arranged evaporators was used to produce gradient films on the basis of the $Ge_{40}S_{60}$ matrix and dopant (Bi, Pb, Te, Al components). The matrix $Ge_{40}S_{60}$ alloy was put into the Knudsen diffusion cell made of molybdenum foil shaped as a parallelepiped with effusion orifices for evaporation. Formation of the dopant atomic beams is provided by the dopant evaporation from additional evaporators. The gradient structure was formed by simultaneous evaporation of the $Ge_{40}S_{60}$ alloy charge in the stationary regime at the evaporator and dopant (Bi, Pb, Te, Al) temperature exceeding by 50–100 K their melting points according to a preset rule of their distribution and film deposition time. In this case, the gradient layer is formed with a uniform or preset modifier distribution over the deposited condensate thickness (0.5–0.25 μm). The condensate was deposited onto glass substrates at the 0.05–0.25 μm/min condensation rate.

It is known [3] that a modifier introduced into the Ge_2S_3 matrix changes substantially the optical and electric properties both during the glass synthesis and during the gradient structure deposition. The studies of the modifier influence on the optical properties of the $Ge_{40}S_{60}$–(Bi, Pb, Te, Al) gradient structures were carried out for the

Table 1. Temperatures and temperature ranges of interaction, crystallization, and melting for the compounds studied

Compd.	Temperature, K			
	Modifier melting	Interaction	Melting	Crystallization
$Ge_{40}S_{60}$	–	–	872–885	855–853
$Ge_{40}S_{60}$–Pb	600.5–610	760–855	880–885	860–857
			890–910	855–847
$Ge_{40}S_{60}$–Al	933–941	718–793	871–888	843–838
		920–933	825–805	–
$Ge_{40}S_{60}$–Bi	543–553	703–805	853–873	815–805
$Ge_{40}S_{60}$–Te	721–733	716–781	833–847	783–760

Table 2. Correlation between refractive index of the compounds and Al and Bi concentration

Composition	Modifier conc., per cent mass	Wavelength, nm	Refractive index	Film thickness, μm
$Ge_{40}S_{60}$	–	750	3.48	1.77
$Ge_{40}S_{60}$ + Al	0.75	750	3.27	1.78
$Ge_{40}S_{60}$ + Al	1.56	750	2.99	2.20
$Ge_{40}S_{60}$ + Al	2.41	750	2.14	2.69
$Ge_{40}S_{60}$ + Bi	–	700	2.06	2.21
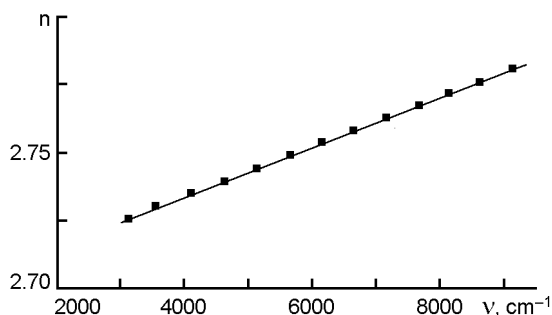
Fig. 1. Dispersion of refractive index *n* for the $Ge_{40}S_{60}$ films.

Fig. 2. Dispersion of refractive index for the $Ge_{40}S_{60}(Te)$ gradient structures with Te content (per cent mass): 5.49 (*1*); 8.0 (*2*); 26.1 (*3*).

films deposited onto glass substrates. The modifiers were selected taking into account the fact that those have both semiconductor (Bi, Te) and metal (Pb, Al) properties. The gradient structures obtained appeared to be amorphous with high mechanical and chemical stability only at a limited concentration of modifiers. Therefore, the optical properties were studied in the concentration ranges of 0 to 11 mass % (Bi), 0 to 10 mass % (Pb), and 0 to 15 mass % (Te) (see Figs. 1, 2 and Table 2). Limitation of the modifier concentration in the $Ge_{40}S_{60}$ matrix could be explained by the peculiarities of micro-non-uniform structure, tendency to possible composition deviation from the $Ge_{40}S_{60}$ stoichiometry and high affinity and energy gain of the modifier and matrix interaction reaction [4].

The increase of the modifier concentration in the $Ge_{40}S_{60}$ matrix is seen to result in the refractive index reduction, perhaps due to disordering of the crystalline lattice frame of the $Ge_{40}S_{60}$ matrix.

Thus, it is shown that under heating at 5 deg/min rate, the interaction of modifiers with the $Ge_{40}S_{60}$ alloy occurs producing new compounds, i.e. the $Ge_{40}S_{60}$-modifier compounds. The technological regimes of the non-uniform gradient thin-film struc-
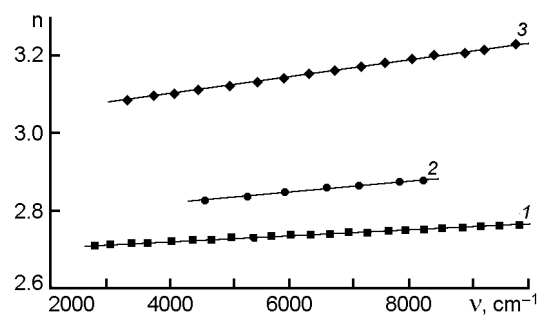
ture preparation have been developed and the transmission and reflection spectra of the structures have been studied. In the transparency region, the dispersion of the refractive indices of thin-film gradient structures has been studied. It has been shown that the enriching of the layers in the modifier (Al, Bi, Pb, Te) causes the absorption edge shift towards longer wavelengths. The increase rate of the gradient film absorption as a function of the incident light energy and the refractive index are decreased. These facts are ascribed to disordering of the crystalline lattice frame of the $Ge_{40}S_{60}$ matrix.

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Одержання неоднорідних градієнтних структур на основі сплавів $Ge_{40}S_{60}$ з модифікаторами

В.Ю.Лоя, А.В.Лада*, С.С.Крафчик, П.П.Пуга, Г.Д.Пуга*

Проведено термографічні комплексні дослідження системи $Ge_{40}S_{60}$-модифікатори (Pb, Al, Bi і Te). Показано, що при їх нагріванні проходить взаємодія модифікаторів із сплавом $Ge_{40}S_{60}$ з утворенням нових сполук $Ge_{40}S_{60}$-модифікатори. Розроблено технологічні умови одержання неоднорідних градієнтних тонкоплівкових структур та досліджено їхні спектри пропускання і відбивання. В області прозорості досліджено дисперсію показників заломлення одержаних тонкоплівкових градієнтних структур.