STUDY OF RECOMBINATION MECHANISMS IN CRYSTALS GaSe DOPED WITH Cu, Cd AND Sn

Ig. Evtodiev[1], El. Cuculescu[1], M. Rusu[2], M. Caraman[1]

[1]Faculty of Physics, Moldavian State University, Kishinev, Moldova
[2]Faculty of Physics, "Al. I. Cuza", University, Iassy, Romania

The energetic diagram of the localized states in the forbidden band energy of the crystals ε-GaSe doped with Cu, Cd and Sn is determined from the analysis of absorption spectra in the field of impurity band, luminescent emissive spectra and thermo luminescent ones.

Introduction

The stratified crystals of GaSe type serve as the basic element in different optoelectronic devices such as the micro lasers (the excitation with the electron beam), optoelectronic modulators for a large domain of wavelengths [1]. In order to enlarge the domain of application of gallium monoselenium and of analogical compounds by the structure and physical mechanical properties (GaS and InSe) it is necessary to increase the variety of characteristic physical properties of these compounds.

The studies of optical properties and photoelectrical ones of the crystals GaS, GaSe and InSe pure nondoped prove that on their base the optoelectronic devices can be elaborated for the visible range and the near IR. In order to reach the conquerable parameters with the existent elaborations (on the base of semiconductors $A^{II}B^{VI}$, $A^{III}B^{VI}$) it is necessary to vary controllably with the diagram of localized states in the forbidden band of these crystals.

It is known [2] that the impurity atoms in the crystals of GaSe type, after the liquidation of structural defects in the sub grid of the metal from the interior of stratified packages Hal-M-M-Hal are localized in the space among the planes of the neighbor packages contributing so to the increasing of cohesion force among packages. These atoms will be situated on the surface of cleaving on the direction perpendicular to C contributing so to the formation of the ionized surface states. The physical properties of the extra fine monocrystalline films are modified by the surface states in which the characteristic properties of the structures with the reduced sizes are manifested.

The method of experiment and the technology of preparation of the samples

The absorption coefficient of the light in the field of impurity bands of the crystals GaSe and GaS is of order 10 cm^{-1} [2]., so in order that the error in the optical determinations does not exceed the order of 5% it is necessary to have the homogenous samples with the thickness of 1 cm. The necessary samples were prepared by cleaving from the homogenous optical monocrystals which were grown by Bridgman-Stockbarger method. The doping of the crystals GaSe with Cu, Cd and Sn was performed in the process of synthesis of the respective chemical compound. The distribution of impurity atoms in the volume of the crystal was established by the method of emission spectral analysis after the characteristic last lines of the respective atoms. The analytical spectra were registered by the spectrograph DFS-8 with the diffraction grating 600 mm^{-1}.

The absorption coefficient α was determined from measurements of spectral dependences of the transmission and reflection of the light from the natural mirror surfaces.

The emissive luminescent spectra and of thermoluminescence were recorded at the combined installation on the base of monochromator MDR-2 with the diffraction grating of 600 mm^{-1} and 1200 mm^{-1}. The luminescence of crystals GaSe was excited with the radiation of laser He-Ne (λ=0.6328 μm, P≈40 mWt), but in the case of thermo luminescence the light source was of Hg steam with the spectrum from the UV domain. The necessary spectral domain for the excitation of luminescence was selected with a set of optical filters.

Experimental results and their explanation

The spectral dependence of absorption coefficient is strongly emphasized by the shape. In the case of transitions valence band – ionized donor at the energies $\hbar\omega \approx E_g^d - E_d^i$ (E_d^i is the energy of ionization of the donor) a line is formed, but in the case of transitions acceptor level with small energy to conduction band the absorption coefficient $\alpha(\hbar\omega)$ is described with the analogical function for the direct optical transitions

$$\alpha(\hbar\omega) = A(\hbar\omega - E_g^d + E_A)^{1/2} \quad (1)$$

where the coefficient A receives the value smaller than the respective coefficient in the case of band – band transition, E_A is the energy of respective acceptor level.

The absorption spectra in the coordinates $\alpha^{1/2}=f(\hbar\omega)$ are presented in fig.1 for the crystals ε-GaSe doped with Cu, Cd and Sn at two temperatures: 78 and 293 K.

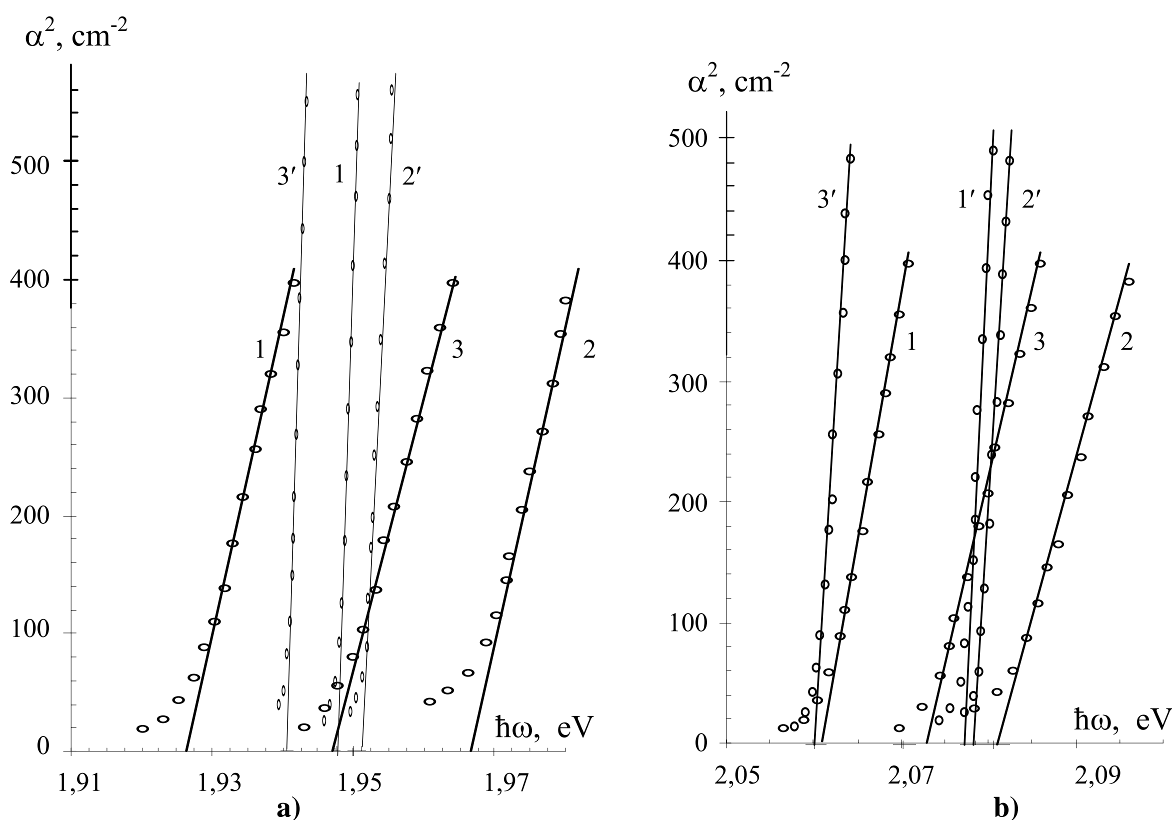

Fig.1. The spectral dependence of absorption coefficient of GaSe crystals doped with Cu (1, 1′); Cd (2, 2′); Sn (3, 3′); 1,2,3 - 0,05% at., 1′,2′,3′ - 0,50% at.;
T, K: a – 293; b – 78.

As we can easily observe the experimental points are arranged on the segments of straight line in accordance with the function (1). Extrapolating the segments of straight line to the value α=0 the energetic interval was determined between the minimum of conduction band and the acceptor level. Knowing the width of forbidden energy band of the crystals ε-GaSe special nondoped and equal to 2.132 eV and 2.037 eV respectively at the temperature 78 K and 293 K the average energy of ionization of the acceptor levels was determined created with Cu, Cd, and Sn, which are values introduced in table 1. As we can see from the table with the increasing of the Cu quantity in GaSe the ionization energy of the respective acceptor is decreased.

Table 1.

Chemical compound, % at.	GaSe: Cu		GaSe: Cd		GaSe: Sn	
	E / E_A, eV (T=78K)	E / E_A, eV (T=300K)	E / E_A, eV (T=78K)	E / E_A, eV (T=300K)	E / E_A, eV (T=78K)	E / E_A, eV (T=300K)
0.05	2.061 / 71	1.927 / 110	2.081/ 51	1.957 / 80	2.073 / 59	1.947 / 90
0.10	2.063 / 69	1.930 / 107	2.066 / 56	1.927 / 110	2.068 / 64	1.945 / 92
0.20	2.070 / 62	1.943 / 94	2.073 / 53	1.942 / 95	2.080 / 52	1.955 / 82
0.50	2.077 / 55	1.948 / 90	2.078 / 58	1.951 / 86	2.060 / 72	1.942 / 95

The photoluminescence spectra of the crystals GaSe doped with Cu, Cd and Sn are presented in fig.2.

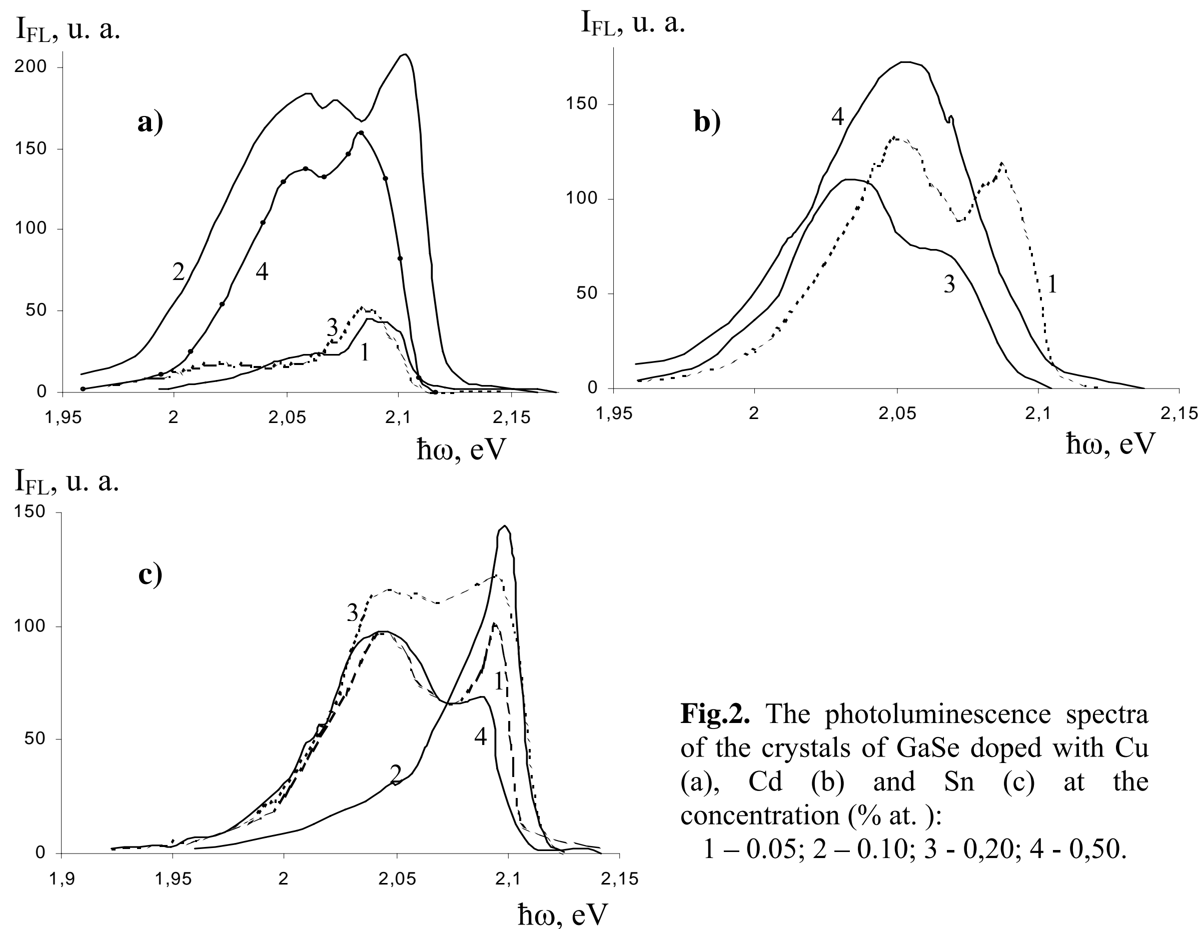

Fig.2. The photoluminescence spectra of the crystals of GaSe doped with Cu (a), Cd (b) and Sn (c) at the concentration (% at.):
1 – 0.05; 2 – 0.10; 3 - 0,20; 4 - 0,50.

The luminescence is initiated in the field of excitonic line n=1 and for all types of samples is composed of two intensive bands localized at red frontier of fundamental band of absorption. The energies of maximal intensity are introduced in tab.2. The excitonic luminescence (n=1) is emphasized clearly in the compounds GaSe with the impurity atoms of Cu in the quantities up to 0.2% at. with a maximum at 2.101 eV. The intensity of this line is in increasing from 0.05% at. of Cu up to 0.1% and further is rapidly decreased which is the fact that allows us to suppose that at small concentrations Cu compensates the structural defects in the subgrid of the metal from the interior of stratified packages. At the concentrations bigger than 0.2% at. copper creates the acceptor levels by which the luminescence band is formed with the maximum at 2.06 ÷ 2.08 eV that correlates better with the impurity absorption spectra (tab.1).

Table 2.

Concentration of the doped substance, % at.		E_1, eV	E_2, eV	E_3, eV	E_4, eV
GaSe: Cu	0.05	2.060	2.088	2.098	2.101
	0.10	2.073	2.092	2.098	2.100
	0.20	2.065	2.089	2.098	2.105
	0.50	2.055	2.080	2.086	-
GaSe: Cd	0.05	2.042	2.08	2.09	-
	0.20	1.990	2.04	2.09	-
	0.50	2.060	-	-	-
GaSe: Sn	0.05	-	-	2.100	-
	0.10	2.04	-	2.098	-
	0.20	2.05	-	2.100	-
	0.50	2.05	-	2.095	-

The doping of GaSe crystals with Cd in quantities from 0.05% at. up to 0.5% at. leads to the formation both of bond centers of excitons which their irradiative annihilation forms the luminescent band with the maximum at 2.08÷2.09 eV and acceptor levels by which the maximum bands at 2.04 ÷ 2.06 eV are created.

The photoluminescence spectra of the crystals GaSe doped with Sn in quantities up to 0.5% are composed of two localized bands at the margin of absorption band. The presence of excitonic line indicates us that the Sn in the small concentrations as Cu liquidates the defects of Ga and forms the acceptor levels localized at ~ 60 meV from the top of valence band.

The energetical diagram of the surface states (capture) in the crystals GaSe doped with Cu, Cd and Sn was established from the thermoluminescent analysis in the interval of temperatures from 78K up to 250 K.

The TLS spectra recorded from researched crystals contain a series of bands, their shapes are in the function of kinetic of TLS [3], of the speed of heating, the number of charge carriers captured on the capturing centers etc. We will take into consideration two limit cases of capturing of nonequilibrium charge carriers and especially:

a) *the linear kinetic of TLS*, for which $\gamma_t N_t << \gamma P_r$, where γ_t is the capture coefficient of the electrons on the capturing centers; γ is the recombination coefficient; N_t is concentration of capturing centers; P_r is the concentration of holes on the recombination centers.

b) *the square kinetic of TLS*, so when the probability of secondary capture of the electrons on the capturing centers is greater than the probability of their recombination on luminescent centers:

$$\gamma_t N_t >> \gamma P_r$$

The theoretical shapes were calculated in paper [4] of TLS spectra for the types of linear and square kinetics. For the linear kinetic the straight of the shape from the domain of low temperatures has a large "stretching "with respect to the domain of high temperatures, but for square kinetic has the inversed symmetry.

The respective temperature is determined by the shape of TLS, its intensity of the band is maximal (T_m); the half-length of the shape of TLS (δ) equal with the temperature differences T_2-T_1 for which the intensity of TLS is ½ from its maximal intensity; the surface (S) margined by the shape of TLS – I(T) and the axis of temperatures.

It is necessary to take into consideration that the form of the shape and the position of the maxima of TLS on the axis of temperatures is influenced both by the kinetic of TLS and the speed of releasing (β_0) of charge carriers from the capture centers at the determination of energy of surface states.

The energies of capture levels determined from the analysis of thermal stimulated luminescence are presented in table 3.

Table 3.

Concentration of the doped substance, % at.		E_t, eV
GaSe: Cu	0.05	0.161; 0.236
	0.10	0.145; 0.148; 0.163; 0.185
	0.20	0.189; 0.337
	0.50	0.147; 0.150; 0.178; 0.228
GaSe: Cd	0.05	0.189; 0.196; 0.516; 0.541; 0.604; 0.710
	0.10	0.185; 0.218; 0.509; 0.544; 0.654
	0.20	0.189; 0.561; 0.601; 0.633; 0.676
	0.50	0.204; 0.246
GaSe: Sn	0.05	0.161; 0.362; 0.370; 0.605; 0.679
	0.10	0.186; 0.376; 0.480
	0.20	0.196; 0.376; 0.199; 0.386
	0.50	0.281; 0.321; 0.343; 0.353; 0.500

Conclusions

The margin of fundamental band of absorption of the crystals GaSe is formed by the optical transitions with the formation of excitonic complexes. The maximum of excitonic absorption line in the state n=1 is localized at 2.102 eV (T=78K). The impurity atoms of Cu, Cd and Sn create the acceptor levels. The energy of created levels of Cu is in the slow decreasing from 110 meV up to 90 meV with the increasing of their concentration from 0.05% at.up to 0.5% at. With the decreasing of the sample temperature from 293 K up to 78 K the energy of acceptor levels of Cu, Cd and Sn is in weak decreasing.

The impurity atoms of Cu in the quantities up to 0.2% at. and of Sn up to 0.1% at. are arranged in the vacancies of Ga from the interior of stratified packages and lead to the

amplification of the intensity of excitonic line n=1 in the photoluminescence spectra. The impurity atoms create the acceptor levels which lead to the formation of the bands in the photoluminescence spectra.

The energetic diagram of the surface states in the crystals GaSe doped with Cu, Cd and Sn in the quantities up to 0.5% at. was established from the analysis of thermal stimulated luminescence.

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