THE CAPTURE AND RECOMBINATION LEVELS ENERGETIC DIAGRAM IN GaSe (Cu) STRATIFIED SINGLE CRYSTALS

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By studying PL spectra, as well photonductivity kinetics and spectral dependences, for different excitation (photon) energies in temperature range 78 K up to ~420 K, energies of localized states due to both Cu and noncontrollable impurities are determined. From comparative annalyse of temperature dependence of electrical conductivity and photoconductivity for undoped and Cu-doped films, the activation energy of acceptor levels was determined as 0.058 and 0.025 eV for GaSe(Cu) films.

***Keywords*:** GaSe, Thin films, Cu impurities, Photoluminescence, Photoconduction

1. INTRODUCTION

At layer surface the valence bonds are practically closed [1], thus leading to low concentrations of surface states. This feature recommends utilization of $A^{III}B^{VI}$ materials as active elements in luminescent diodes (LEDs) and micro-lasers in VIS and NIR spectral domains [2, 3].

The electrical, photoelectrical and luminescent properties of Cu doped GaSe (concentrations up to ~ 0.50 % at.) single crystals have been studied for to determine the energetic states induced by Cu atoms and intrinsic defects.

2. EXPERIMENTAL

The GaSe single crystals were grown from melt (Bridgmann's method) in a temperature gradient furnace. Cu atoms in proportions of 0.01-0.50 % at. have been introduced into the initial element composition for the chemical synthesis.

The photoluminescence (PL) spectra of GaSe (Cu) crystals at 78 K have been excited by N_2 laser (λ=334 nm) and a DRS-500 Hg lamp (λ=546 nm). The energy spectrum of capture levels has been studied by using the thermally stimulated currents (TSC).

3. RESULTS AND DISCUSSION

The GaSe *a* and *c* parameters of the hexagonal lattice have been determined from CuK_α (λ=0.15418 nm) XRD patterns (Table 1). The above results can be interpreted by taking into the account that the covalence radius of Cu is lesser than that of Ga, and thus by filling Ga vacancies with Cu atoms (relatively low proportions), the lattice practically doesn't change.

The temperature dependencies of the electrical conductivity for undoped (curve 1) and Cu-doped GaSe with impurity concentrations in the range 0.01-0.20 % at. (curves 2-4) is show in Figure 1.

Table 1.

Cu concentration, % at.	0.00	0.01	0.05	0.10	0.20	0.50
a, Å	3.752	3.752	3.757	3.765	3.767	3.767
c, Å	15.952	15.951	15.949	15.950	15.948	15.946

In temperature range (78-300) K, the electrical conduction of undoped GaSe crystals is determined by two acceptor levels located at ~70 meV and 130 meV, respectively, toward the top of the valence band (Figure 1, curve 1).

Cu-doping of ε-GaSe crystals up to 0.1 % at. leads to the formation of a new acceptor level, located at about 90 meV toward the top of the valence band. One can consider that by liquidating structural defects in the metal sublattice (inside stratfied package), Cu atoms fill up the acceptor levels with energies of 70 and 130 meV, and create a new acceptor level assembly with an average energy of 90 meV (Figure 1, curves 2-4).

By increasing the concentration of Cu over 0.20 % at., the level by 90 meV maintains, besides a new type of deep localized states, positioned at 210 meV against the top of the valence band, shows up. This is a deep acceptor level, produced by Cu impurity atoms, located between halogen plans of neighbouring packages.

By analyzing the thermally stimulated currents (TSC) and photoluminescence (PL), the characteristics of these levels are to be determined. The temperature dependence of the TSC, I_{TSC}=f(T), for Cu-doped GaSe samples with an impurity amount in the range (0.01-0.50) % is showed in Figure 2. The J_{TSC}=f(T) curves show several bands with well outlined maxima. The energy of capture levels for 0.01÷0.50 % at. Cu doped GaSe are determined by the maximum of $J(T)$ plot and from the slope of $\lg J = f\left(10^3/T\right)$ plot and are given in Table 2.

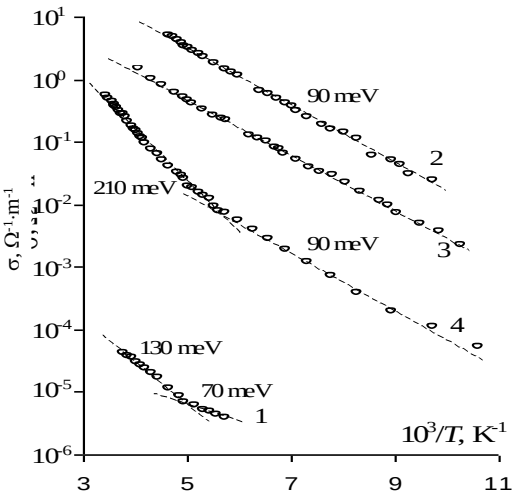

Figure 1. Temperature dependence of the dark electrical conductivity for undoped GaSe (1) and Cu-doped GaSe with Cu concentration 0.05 % at. (2), 0.10 % at. (3) and 0.20 % at. (4).

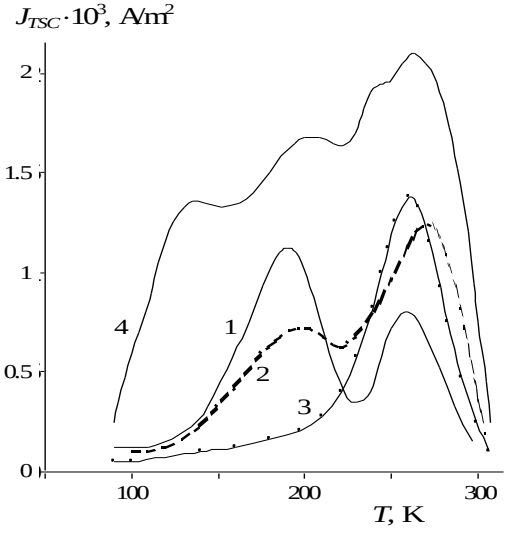

Figure 2. Temperature dependence of TSC for Cu-doped GaSe. 1 – 0.01 % at.; 2 – 0.05 % at.; 3 – 0.10 % at.; 4 – 0.50 % at.

Table 2.

Cu concentration, % at.	0.00	0.01	0.05	0.10	0.20	0.50
Energy of the capture levels, eV	0.32	0.38	0.40	-	0.28	0.26
	0.51	0.52	0.54	0.52	0.49	0.40
	(0.53)					0.47
						0.53

As one can see from Table 2, the capture level with 0.52 eV (average) energy is present in samples with all range of doping concentrations.

The spectral dependencies of photoluminescence (PL) for GaSe (Cu) crystals at 78 K are presented in Figure 3. The PL spectrum of undoped crystals consist of two bands, one characterized by a structured contour located by 2.09-2.10 eV, while the other, a broad band, is of impurity nature and is positioned at ~2.03 eV. The first band is splitter in two components peaked at 2.092 and 2.097 eV.

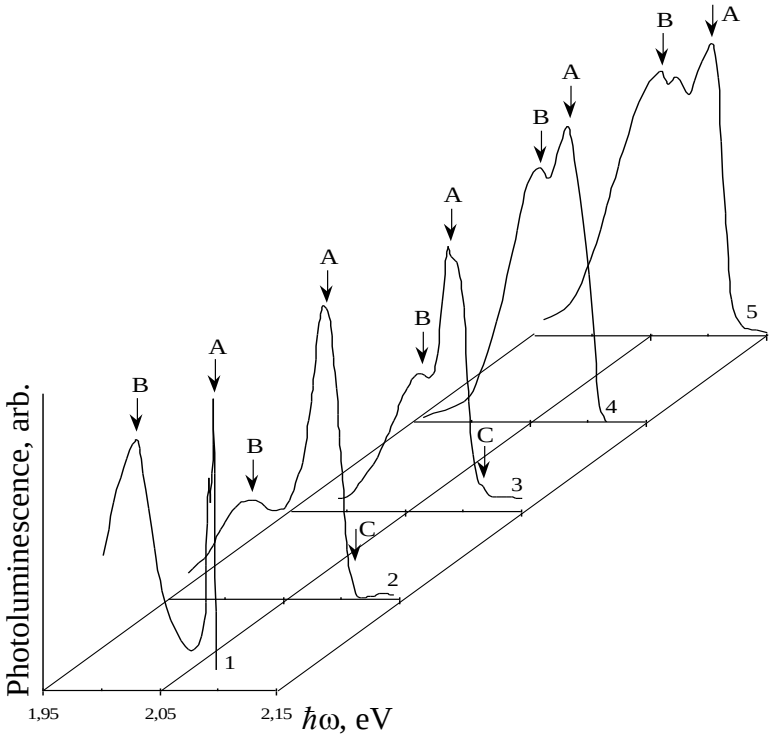

Figure 3. Spectral distribution of PL for undoped (1) and Cu-doped GaSe (2 – 0.05 % at.; 3 – 0.10 % at.; 4 – 0.20 % at.; 5 – 0.50 % at.) at temperature 78 K.

The spin-orbit splitting for state n=1 excitons state, is of the order of 2 meV [4] and, consequently, smaller than the energy interval between the excitonic peak components. The 2.097 eV peak is associated with free excitons annihilation and the 2.092 eV peak - is due to the radiative annihilation of the excitons bounded to ε-GaS crystal ionizing centers with a ~5 meV binding energy.

Taking into consideration, that holes are the majority charge carriers in both undoped and Cu-doped GaSe crystals (up to 0.0 % at.), the band at 2.03 eV can be assigned to the luminescent recombination of the non-equilibrium charge carriers from the conduction band with the holes localized on acceptor levels, 90 meV from the valence band top.

As is evidenced in Figure 3, Cu impurity atoms do modify the structure of the radiative spectrum. At low concentrations (~0.05 % at.), the peak of the impurity band displaces toward higher energies by ~30 mV as against respective band in undoped crystals, while the outer band has three components with maxima at 2.088, 2.098 and 2.113 eV. The maximum by 2.098 eV corresponds to the radiative annihilation of the free excitons in the state n=1, while the (weak) particularity by 2.113 eV can be associated with the radiative annihilation of the excitons in the state n=2. The last two particularities coincide (as energy position) with respective lines from the absorption spectra of ε-GaSe crystals at low temperatures. The particularity with energy 2.088 eV can be associated with the radiative annihilation of the bond excitons (binding energy equal to ~10 meV).

An increased Cu concentration up to 0.20 % at. result in an enhanced impurity PL, as can be seen in curves 3 and 4. Cu addition leads to the increase in the concentration of recombination levels localized by 60-65 meV against the top of the valence band.

Further increasing Cu concentration up to 0.50 % at., the band of free excitons gradually extinguishes, but a new band with maximum at 2.073 eV shows up, which is displaced toward lower energies by ~26 meV as compared with the line of the free excitons. It is associated to the radiative annihilation of free excitons, accompanied by LO phonon emission, with an energy of ~26 meV [5].

At increased temperatures above 78 K, the intensity of the exciton band decreases, while the impurity band B initially enhances and reaches the peak value at about 150 K, afterwards it quenches exponentially.

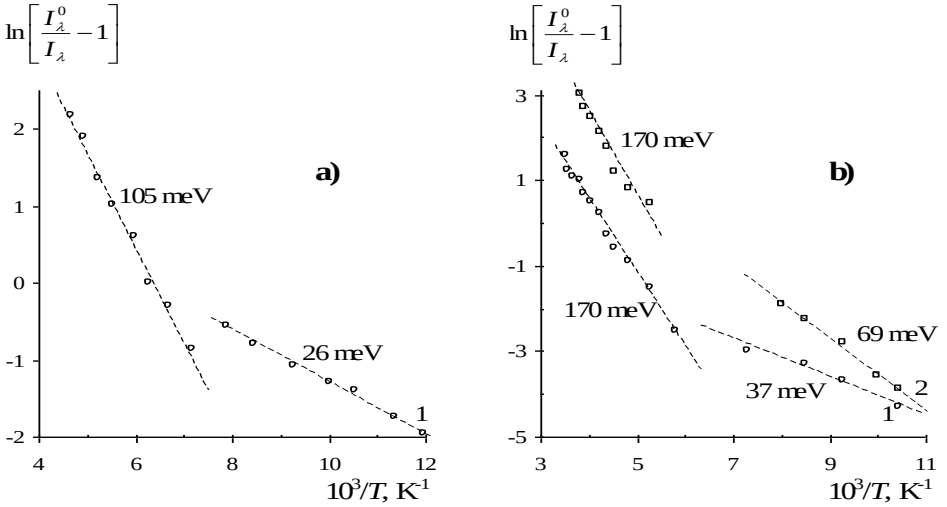

Figure 4. *Temperature dependence of the peak PL intensity for bands A (1) and B (2) in GaSe(Cu) crystals. Cu, % at.: 0.05 (a) şi 0.10 (b). Indicated are the values of the activation energy.*

The dependencies of the peak intensity for the bands A and B in function of the reciprocal temperature are presented in Figure 4, for two Cu concentrations. For low Cu concentrations, the energy

of thermal ionization of the band A is about 26 meV. The recombination level, determining the B PL band, is localized at ~105 meV from the valence band top.

Increasing Cu doping of GaSe up to 0.50 % at., the exciton band probably merges the impurity band and forms a mixted band. The average energy of the respective impurity level is equal to only ~11 meV toward the top of the valence band. For this reason the nature of quenching for the band A at increasing temperature coincides with PL quenching of the free excitons in undoped GaSe crystals. The average energy of the recombination level created by Cu atoms (0.50 % at.) is about 0.17 eV.

4. CONCLUSIONS

The electrical conductivity of GaSe(Cu) crystals depends on both temperature and Cu concentration. The accidental impurities produce two acceptor levels in the GaSe forbidden band, with thermal ionization energy of about 70 and 130 meV, respectively. Cu atoms at low concentrations, under 0.10 % at., create a new acceptor level with an average energy of 90 meV.

From the analyses of TSC the energies of the capture levels for undoped and Cu-doped up to 0.50 % at. have been determined. At increased Cu concentration up to 0.05 % at., the average energy of the surface levels increases; for higher concentrations (0.20% at. and 0.50% at.), a new energy band diagram is effective.

The complex structure of the PL band is due to the radiative annihilation of free excitons in n=1 (the peak at 2.098 eV) and n=2 (the peak at 2.113 eV), as well as of bounded excitons (to ionizing centers) with a binding energy of ~10 meV. Besides, Cu atoms create a ~105 meV recombination level.

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