THE STUDING OF PHOTOCONDUCTION MECHANISM OF THE PHOTOSENSITIVE CRYSTALS BY THE TYPE OF $PbGa_2S_4(Se_4)$

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The photosensitive structures of $In/PbGaS_4$ and $In/pbGaSe_4$ have been created and investigated. the spectral dependencies of photocurrent at the different temperatures and applied voltages, show the presence of the local centers inside the forbidden band width, connected with the self-doping and appearing crystals in the process of the obtaining.

The numerous class of the triple compounds $II\text{-}III_2\text{-}IV_4$ (where II two-valent cations are Mn, Pb, Hg, Zn; III three-valent are chalcogens S, Se), belong to the number of multicomponent semiconductors, the initial investigations of which have already led to new besides them, which are perspective for the applying of the materials in the optoelectronics [1,2].

The compounds $PbGaS_4(Se_4)$, belonging to the given class, are the photosensitive ones in the visible region of the spectrum. Some parameters of crystals (the forbidden band width, the nature of the optical transitions, phonon energy, dielectric constant, photoconduction mechanism and e.t.c.) were identified by the investigations of their physical properties, in the same way as the electric and optical ones (absorption and Romanov spectrums) [3-5].

In the present paper the results of the investigations for the studying of the photoconduction nature in $PbGaS_4(Se_4)$ are presented.

On the basis of the experimental and literature data, we can note, that $II\text{-}III_2\text{-}VI_4$ belong to the defective crystal group. The wide application of the semiconductors $II\text{-}III_2\text{-}VI_4$ in the microelectronics during long time was strongly limited by fact, that in these semiconductors always many prolonged defects, such as boundaries of grains and dislocation. It is known, that such defects are responsible not only for the significant decrease of the motion of majority carriers and the life time of the minority carriers, but can be as the centers of the creation of the secondary phases and segregation of impurities in the process of the crystal growth [6].

Thus, the significant change of these material properties can be achieved by the way of the controlled doping, i.e. that in the process of the crystal growth the degree of their inclination from stoichiometric can be controlled or influenced on the segregation impurity mechanism.

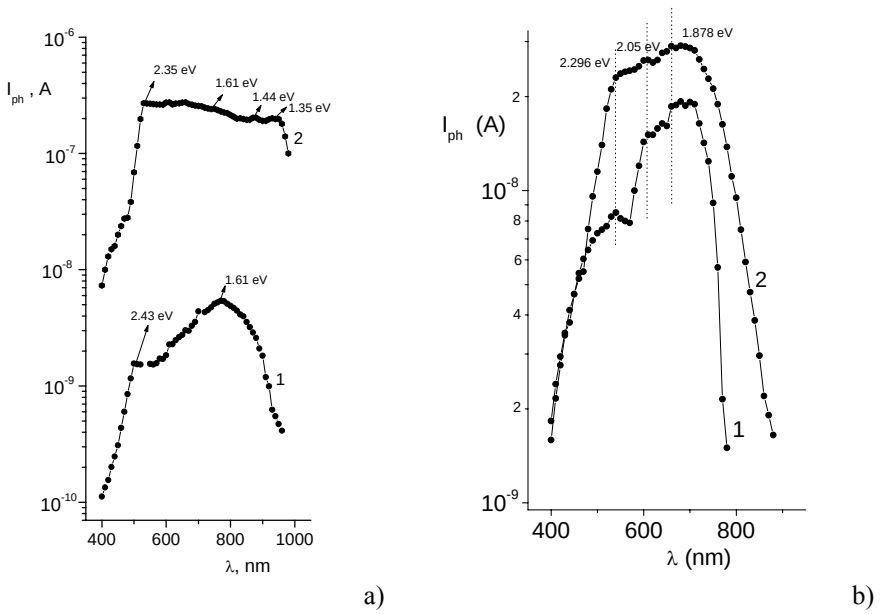

Fig.1. a) The photoconduction spectrum for the structures $In/PbGaSe_4$ at the temperatures T=110(1), 306K(2).
b) The photoconduction spectrum of $In/PbGaS_4$ at the temperatures $In/PbGaS_4$ at the temperatures T=100(1), 290K(2).

The obtaining of the detailed know ledges about local disorder, as in the elementary semiconductors, so in the compounds, is the open problem, as disordered mass impurities or point defects in some crystal region difficultly differ from the prolonged ones. The prolonged defects are the sources of the electric fields and fields of the high voltage, appearing near them, that significantly differs their electronic states from the electronic states of the local mass of

impurities. It can be proposed, that photoconduction in the crystals PbGaS4 and PbGaSe4connects with such prolonged defects, which manage to store the big enough charge for the illumination time. It is hardly to believe, that the permanent impurities, being in the substitution state or the intrinsic point defects can influence on the band structure so significantly, i.e. lead to the appearance of the local electronic stats inside the conduction band. In this case in the photoconduction band the maximums would be appeared behind the intrinsic absorption edge (fig.1a and 1b).

From the figures it is seen, energetic value of short-wave maximum on the photoconduction spectrum samples of $PbGa_2Se_4$ coincides to the value, defined from the measurements of the optical absorption (E_g=2,35eV) [4], but on the photoconduction spectrums of $PbGa_2Se_4$ samples the intrinsic conduction band isn't observed. However, the optical absorption edge for the direct allowed transitions shows that E_g=2,78eV [7].

At the low temperatures the spectrum narrower and the impurity maximum at 1,61eV becomes more intensive than the short-wave one, but the other maximums disappear. This fact probably connects with the insufficient influence of such kinds of defects on the conduction at the low temperatures. In the samples PbGa2S4 the temperature decrease doesn't lead to the decrease of the action of the similar kinds of defects that probably connects with the decrease of the defect number, taking part in the conduction.

For the observation of the effects, which go on the crystal volume of $PbGa_2Se_4$, the samples were lightened from the opposite side of contact (fig.2). It is seen, that at this the intrinsic photoconduction band becomes almost invisible on the phone of the impurity conduction bands. This fact and moreover, the difference of the energetic positions of the maximums, by our opinion connects with the quantity and different volume impurity distribution.

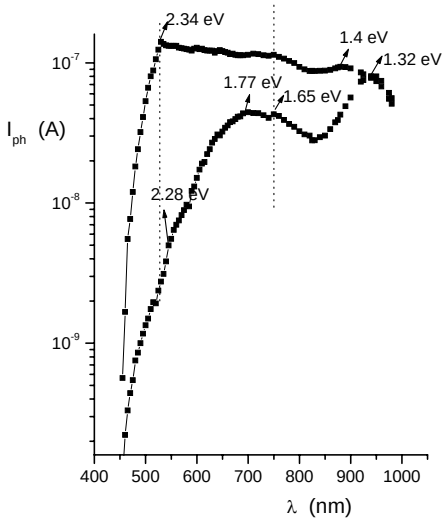

Fig.2. The photoconduction spectrum of $PbGaSe_4$ at T=300K. The illumination geometry: from the side of indium contact – 1; from the side of $PbGaSe_4$ crystal – 2.

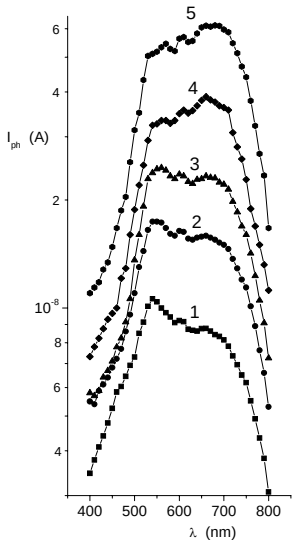

Fig.3. The photoconduction spectrums of In/$PbGaS_4$ at 300K and applied voltage U=50(1), 100(2), 250(4), 400(5).

The analysis of the obtained experimental data shows that energetic position of the maximums on the photoconduction spectrum for the sample In/$PbGaS_4$ doesn't depend on the external electric field and temperature (fig.3).

The observation of these defects connects with the realization in the base region of the structures of the complex (multicentral) recombinative model, including the *s*-channel of the intensive recombination, *r*-centers of photosensitivity, *t*-centers of majority carrier attachment [8].

As the *r*-centers are the photoactive, so they cause the more slow temp of electron recombination, and consequently the most time of their life

$$\tau_n = \frac{g_r}{C_{nr} P_r}$$

where $g_r \sim C_{pr} N_r$ realizes between regions of the temperature extinction of photocurrent (TEPh) and temperature activation (TAPh) and depends on the yield of the recombinative flux on *r*-channel ($g_r \leq 1$); C_{nr} and C_{pr} are the coefficients of the electron and hole capture by slow *r*-recombinative centers, N_r and P_r are concentrations of electrons and holes on *r*-levels at the illumination.

The intensity of the impurity band (fig.4), connected with *r*-centers is proportional to the value $\tau_n(3)$ under the condition $g_r=1$. They depend on the technology of crystal obtaining.

The regions of TAPh (100÷131K) and TEPh (131÷250K) are observed on the temperature dependence at the impurity excitation of monocrystal sample $PbGaS_4$.

At the temperature (131K), according to the photocurrent maximum, the main recombinative flux goes through r-centers. The further temperature decrease leads to the generation of the minority carriers from *r*-centers and promotes to the transition of these charges on *s*-centers, with the connection of which, the life time of the free electrons decreases and TEPh is observed.

Using the method, described in the ref [9], based on the experimental data, the energetic state of the *r*-centers of recombination, which is equal to 0,24eV, has been defined.

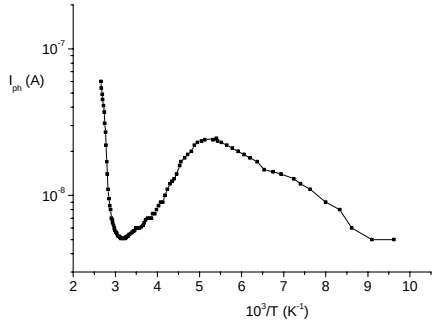

Fig.4. The dependence on the photocurrent temperature for $In/PbGaS_4$.

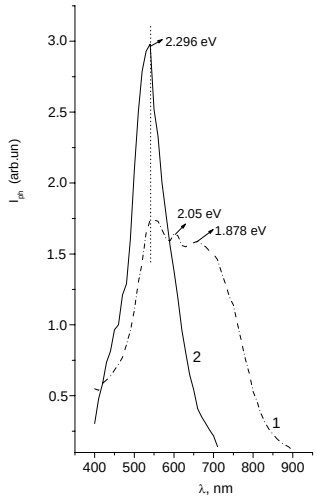

Fig.5. The photoconduction spectrums of $In/PbGaS_4$ before (1) and after annealing (2).

On the fig.5 the photoconduction spectrums before and after crystal annealing with and without sulfur atmosphere are presented. It is seen, that annealing leads to the disappearance of the another types of th defects besides the one. This proves the presence of the defective structure and in spite of the quantity of the defects this doesn't lead to the appearance of the secondary phase that is proved by differential-thermal (thermographical) analysis (fig.6).

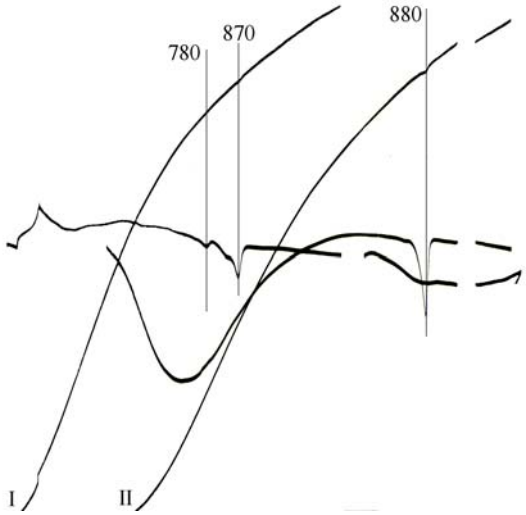

Fig.6. The thermographical spectrum of $PbGaS_4$ crystal before (I) and after annealing (II).

In the conclusion we can note, that photoelectrical active centers in $PbGa_2S_4$ and $PbGa_2Se_4$ can be intrinsic defects – vacancies of atoms of sulfur and selenium, correspondingly, appearing in the result of these atoms from the composition in the synthesis process. Quantity of these defects is correlated by the technological modes of crystal obtaining.

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$PbGa_2S_4$ (Se_4) TİPLİ FOTOHƏSSAS KRİSTALLARDA FOTOKEÇİRİCİLİYİN MEXANİZMİNİN ARAŞDIRILMASI

$In/PbGa_2S_4$ və $In/PbGa_2Se_4$ structurları yaradılmış və tədqiq edilmişdir. Müxtəlif temperaturlarda və tətbiq olunan gərginliklərdə spektral asılılıqlar qadağan olunmuş zolağın üzərində kristalın alınması zamanı əmələ gələn və özü-aşqarlama ilə əlaqədar olan lokal mərkəzlərin mövcudluğunu göstərir.

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ВЫЯСНЕНИЕ МЕХАНИЗМА ФОТОПРОВОДИМОСТИ У ФОТОЧУВСТВИТЕЛЬНЫХ КРИСТАЛЛОВ ТИПА $PbGa_2S_4(Se_4)$

Созданы и исследованы фоточувствительные структуры $In/PbGaS_4$ и $In/PbGaSe_4$. Спектральные зависимости фототока при разных температурах и приложенных напряжениях указывают на наличие локальных центров внутри ширины запрещенной зоны, связанных с самолегированием и возникающих в процессе получения кристаллов.

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