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PHOTOLUMINESCENCE OF EPITAXIAL FILMS OF $Ga_XAL_{1-X}P$ DOPED BY VARIOUS CONCENTRATIONS OF ZINC AND TELLURIUM

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ABSTRACT. The effect of zinc and tellurium ligature on photoluminescence spectra has been studied in a large quantity of epitaxial films $Ga_xAl_{1-x}P$. It was found that inclusion of zinc or tellurium in large quantities in $Ga_xAl_{1-x}P$ films causes the attenuation of the green luminescence and photoluminescence origination in the red area of spectrum simultaneously. We were the first to reveal this phenomenon in this system. As the reason of the formation of these two parallel processes we consider technological defects as well as recombination and annihilation processes proceeding on acceptor and donor levels of zinc and tellurium, respectively. The dependence of changes of intensity of the green luminescence on the quantity of acceptor and donor impurities has been expressed graphically.

$Ga_xAl_{1-x}P$ are very interesting and promising semiconductor materials in optoelectronic instrumentmaking industry. These mixed crystals are notable for the forbidden gap increase with aluminum addition to GaP and at the same time for a shift to short wavelengths of yellow luminescence characterizing GaP. As a result it is possible to receive a green luminescence in this system. Optical properties of this system are insufficiently explored, so we continue the purposeful study of the above semiconductors in the mentioned direction.

The aim of the given work is to study photoluminescence in epitaxial films of various types to determine photoluminescence mechanisms and conditions in the films, where green luminescence is optimal. It is important to study the influence of Te and Zn ligatures included in various concentrations in $Ga_xAl_{1-x}P$ on photoluminescence spectra.

Many epitaxial films of various kind and origin were at our disposal. They all were synthesized with liquid-phase epitaxy. Graphite boat was used as a reactor. Epitaxy process was produced at 970^0C temperatures. Deposition was carried out on both *n*-type and *p*-type GaP substrates surfaces, orientation of which was mainly (001). There were undoped films giving n-type conductivity; *n*-type films doped with tellurium impurity and that of *p*-type doped with zinc impurity.

Recording of photoluminescence spectra was made with the same laboratory setup by which we were recording Raman spectra [1]. Double diffraction spectrometer DFS-24 served as a spectrometer. Registration was carried out by photon counting and synchronous detection methods. Photomultiplier FEU-79 served as a signal detector. We produced photoluminescence excitation by 514.5, 488.0Å wavelengths of argon ion laser radiation and 441.6Å of helium-cadmium laser radiation. All measurements were carried out at room temperature. Epitaxial film thickness was about 10-16 µmc though we had thicker films too.

Fig.1 shows photoluminescent spectra of undoped, tellurium-doped and zinc-doped $Ga_{0.68}Al_{0.32}P$ (by 488.0 nm excitation). The green luminescence characteristic peak is seen in all the three samples. Green luminescence of undoped film is observed at 540.0 nm. When doping with a few quantity of tellurium the green luminescence is shifted to long waves and observed at 542.0 nm; but in case when films are doped with a few quantity of zinc the green luminescence is shifted to longer waves and the characterizing peak is at 545.0 nm. In all the three cases there is no long wave luminescence - a red luminescence near 1.94-1.97 eV` in the photoluminescence spectrum; the fact probably denotes comparatively good quality of films, negligible quantity of defects and deep levels. In connection with this it should be noted that in $Ga_{0.68}Al_{0.32}P$ the green luminescence intensity of undoped films is slightly greater than that of doped films with a few quantity of tellurium, while introduction of a few quantity of zinc causes sharper increase of the green luminescence.

All epitaxial films of various types studied by us without exception show green photoluminescence, the intensity of which is being changed over the great range according to film composition

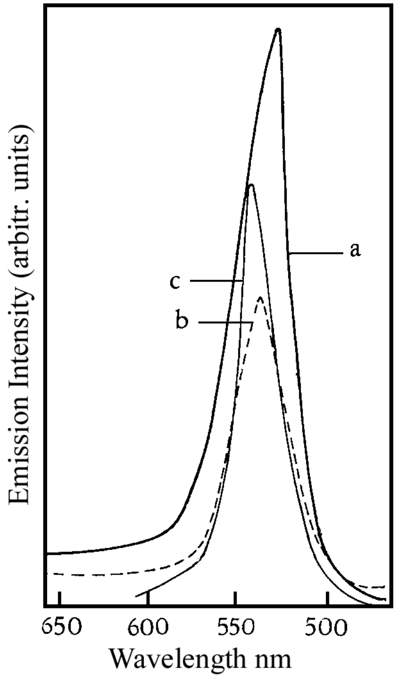

Fig.1. PL spectra for undoped (a), tellurium-doped (b) and zinc doped (c) $Ga_{0.68}Al_{0.32}P$ with 488.0 nm excitation

(x-value), carrier concentration in certain compositions, types of these impurities and degree of structural perfection of these mixed crystals. For example, in mixed crystals $Ga_{1-x}Al_xP$ that are doped with 20 mg zinc, the intensity of green photoluminescence is decreased by the ratio of about 111:11:25:1, when aluminum concentrations are changing in succession of x = 0.06, 0.32, 0.5, 0.68, accordingly. Thus green luminescence is great when a few quantity of aluminum is introduced in GaP and then it falls with aluminum concentration increase. The halfwidth of the peak characterizing the green luminescence is 25- 30 nm. The energetic position of green luminescence peak changes sharply with mixed crystal composition change. This relation is shown in Fig.2.

We have studied films of various compositions but in view of studying the concentration dependence of acceptor ligature of zinc we have selected films of three various compositions: $Ga_{0.66}Al_{0.34}P$, $Ga_{0.42}Al_{0.58}P$, $Ga_{0.35}Al_{0.65}P$. Each of these compositions was doped by zinc ligature in the following quantity: 5, 10, 20, 30, 40, 60, 90 and 100 mg.

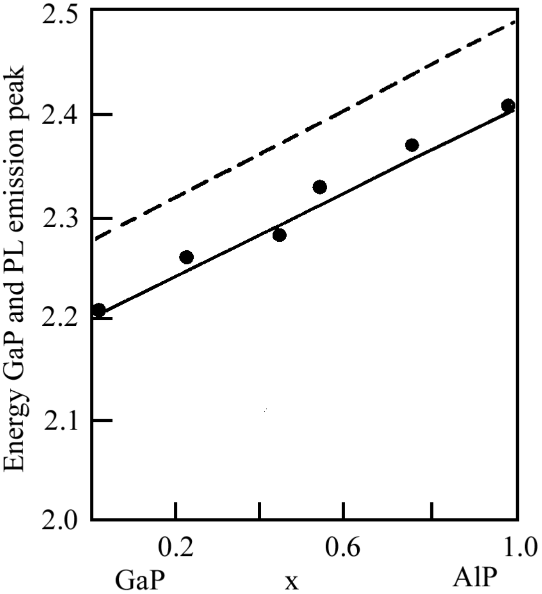

Fig.2. Dependence of the energy of the spectral peak characterizing the green photoluminescence for $Ga_xAl_{1-x}P$ on epitaxial film composition

Fig.3 shows photoluminescence spectra of $Ga_{0.66}Al_{0.34}P$ mixed crystal, when 5, 60 and 90 mg zinc is included in the film. The spectra show clearly gradual attenuation of green luminescence, the corresponding peak of which is at 545.0 nm. Simultaneously red luminescence is originated at 1.973 eV. The green luminescence changes according to composition and Fig.2 shows this process. The position of red luminescence peak is practically invariable.

Fig.3 shows that for composition $Ga_{0.66}Al_{0.34}P$ the intensity of green luminescence decreases after addition a great amount of zinc (above 40 mg). In case when zinc amount does not exceed 40 mg (not shown in Fig.3) the intensity of green luminescence increases a little, reaches maximum and then decreases above 40 mg.

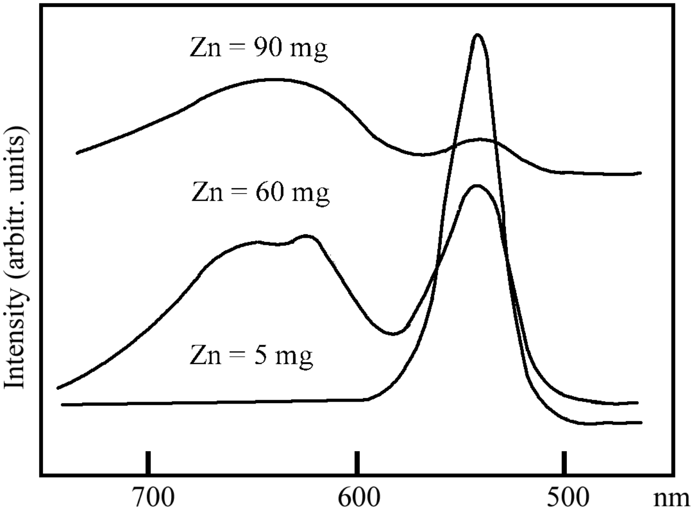

Fig.3. PL spectra of epitaxial films $Ga_{0,68}Al_{0,32}P$ for various concentrations of zinc; λ_L= 488.0 nm

For composition $Ga_{0.42}Al_{0.58}P$ the increase of zinc ligature amount causes monotonous attenuation of green luminescence and origination of red luminescence. In case of $Ga_{0.35}Al_{0.65}P$ at increase of zinc amount green luminescence decreases for a while, then increases in a certain interval of growth of zinc amount and afterwards decreases again when amount of zinc increases. These results are shown in Fig.4.

It turned out for Zn-doped films (to 40 mg) that green luminescence intensity decreases in parallel with increase of aluminum concentration. The experimental fact is shown in Fig.5.

We have studied three films of various compositions during tellurium-doping: $Ga_{0.68}Al_{0.32}P$, $Ga_{0.46}Al_{0.54}P$, $Ga_{0.35}Al_{0.65}P$. Each composition was doped by four various quantities of tellurium: 1, 4, 10 and 20 mg.

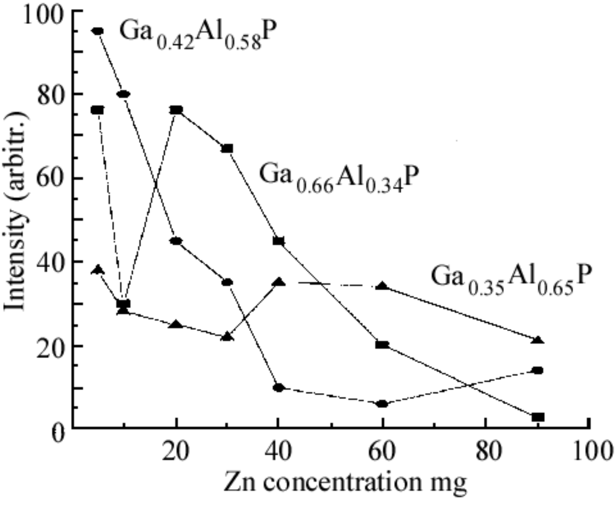

Fig.4. Dependence of intensity of the spectral peak characterizing the green photoluminescence for $Ga_xAl_{1-x}P$ on the concentration of zinc for the three different compositions of films

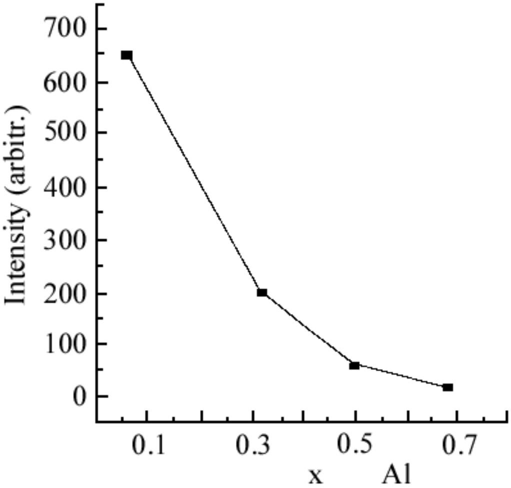

Fig.5. Dependence of the green luminescence intensity on aluminum quantity in the films $Ga_xAl_{1-x}P$

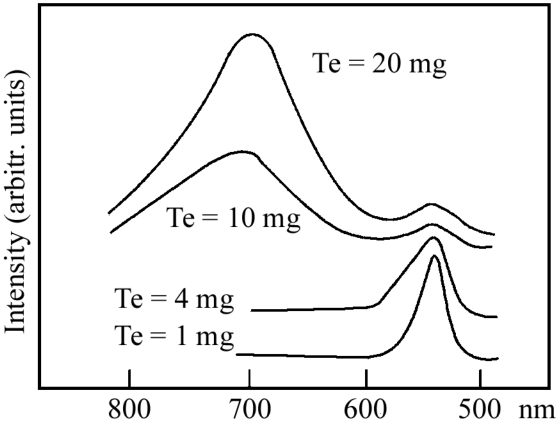

Fig.6. PL spectra of epitaxial films $Ga_{0,68}Al_{0,32}P$ for four various concentrations of tellurium; λ_L=488.0 nm

Fig.6 shows photoluminescence spectra for $Ga_{0.68}Al_{0.32}P$ composition when the ligature concentration varies according to tellurium quantity mentioned above. The spectra show clearly that the green luminescence is observed distinctly at all tellurium concentrations. The luminescence peak for a given composition is situated near 2.3 eV and its intensity is great when tellurium doping occurs up to 10mg. When tellurium ligature quantity increases (10, 20 mg), decrease of green luminescence peak intensity is observed clearly. Simultaneously formation of a new peak in red region of spectrum about 1.72 eV is observed. One may conclude that two parallel processes are occurring: the green luminescence disappears gradually and at the same time the red luminescence is being originated as tellurium ligature increases.

Almost the same picture is observed in case of two other epitaxial films of different compositions. The distinction among compositions is observed in cases when aluminum concentration increases. For instance, in case of the same quantity of tellurium ligature the green luminescence intensity decreases at increase of aluminum concentration. On the contrary, the red luminescence becomes more distinct for large compositions of aluminum.

The green luminescence peak position varies linearly according to mixed crystal composition; this is shown in Fig.2. But red luminescence peak position on the energetic scale is almost invariable according to composition.

Based on experimental data, Fig.7 shows graphs which represent a dependence of green photoluminescence intensity on tellurium ligature quantity.

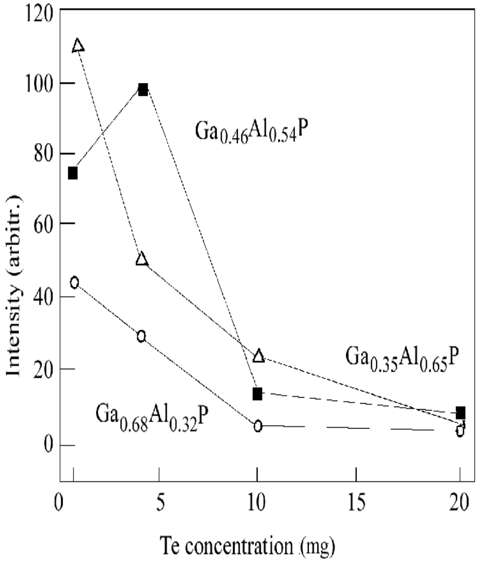

Fig.7. The dependence of the intensity of the spectral peak characterizing the green photoluminescence for $Ga_xAl_{1-x}P$ on the concentration of tellurium for the three different compositions of films

Undoped films of various compositions also have been studied (about twelve films). All the undoped films display electric conductivity. Photoluminescence spectra of each specimen give the green luminescence, intensities of which are about the same as green photoluminescence intensities of 1-4 mg tellurium-doped films. The red luminescence is noted only in some films and as in case of tellurium-doped films, the green luminescence attenuation process in undoped films proceeds simultaneously with the red luminescence origination.

As to red luminescence peaks, their energetic position almost does not change with mixed crystal composition change. It must be noted that long wave luminescence peaks in undoped, tellurium-doped and zinc-doped films are arranged at various wavelengths.

Partially these are 1.76 eV, 1.797-1.72 eV and 1.81-1.97 eV in energetic units accordingly. In undoped films this red luminescence is observed in some specimens; but in case of tellurium and zinc doping it is always observed with various intensity above carriers of certain concentration.

The graph in Fig.2 is plotted for *p*-type films, when during epitaxy process 5 mg zinc is added to mixed crystals. At the same time this Figure shows optical forbidden gap dependence on the composition for this system. It is plotted according to [2]. Evidently this dependence is energetically higher than photoluminescence peak dependence graph. We can conclude from this that green luminescence of films is not caused by the recombination of free carriers, zone-zone mechanism, but its origination is connected with the acceptor-donor pair recombination. Probably Si (A)-Te (D) serves as the above mentioned pair in case of *n*-type films while in case of *p*-type – Si (D)-Zn (A). Silicon impurity is included in films from the reactor and it is an uncontrolled impurity. In undoped films donor-acceptor pair stimulating luminescence probably are uncontrolled impurities and it is very likely that Si (D)-C (A) pair plays that part.

It is more complicated to explain the mechanisms causing red luminescence. There are different opinions. Some consider recombination radiation on Si (D)-Si (A) as a red luminescence mechanism. According to other’s opinion the luminescence cannot be produced by donor-acceptor pair recombination and they consider a possible mechanism causing red luminescence, defects near heterotransition region, which are produced because of distinction between GaP and AlP lattices (before they were thought identical due to incorrect measurement).

As we partially mentioned above, on the basis of our experiments we have not detected red luminescence in films of some composition, type and containing certain carrier concentration, whereas the green luminescence of great intensity is observed easily; moreover, we were the first to study photoluminescence dependence on carrier concentration in $Ga_{1-x}Al_xP$ system and to reveal that when electron or hole concentration is changed in this system by tellurium or zinc-doping, after a certain concentration in both cases the green luminescence slowly decreases until saturation of a certain level and simultaneously the red luminescence is originated. It should be noted that in films of a certain composition the red luminescence is presented by a single peak, sometimes there are two peaks of the red luminescence with different wavelengths. We were the first to reveal for this system that when ligature concentration increases green luminescence decrease is observed and simultaneously a red photoluminescence is originated.

On the basis of the above mentioned experiments and facts we can say certainly that in $Ga_xAl_{1-x}P$ system technological defects cause a red luminescence. These defects are of several types: uncontrolled impurities; structural defects, including stresses formed during heterotransitions; I would like to underline the third mechanism, the recombination channels during the red luminescence, that are formed in case of tellurium or zinc-doping. It is clear, that peak quantity, intensities and their half widths corresponding to the red luminescence, are reliable and exact parameters of technological processes perfection for the mentioned semiconductor system and of the quality of the resultant films, correspondingly. That is, in case of perfect film we must not have the red luminescence; and then the green luminescence achieves maximum. The fact proving nonexistence of composition gradient through the total thickness of the film will be minimal magnitude of the green luminescence peak halfwidth.

Thus we have showed directly that explanation of the red luminescence by defects formed due to the incompatibility of two different lattices is wrong and it is necessary to account those recombination channels which are formed from deeper impurity levels and which are connected to specially introduced zinc or tellurium acceptor or donor levels, correspondingly.

As the films under investigation were synthesized on GaP substrate, we consider it reasonable to eliminate the version according to which the red luminescence we had revealed in ternary epitaxial films, was generated from GaP. It is known that GaP is characterized by luminescence in red and yellow areas according to the impurity included in it. Fig.8 shows PL spectra excited by 488.0 nm wavelength for S-doped, Te-doped and Zn-doped GaP. Table1 shows wavelengths of maxima corresponding to wide bands characterizing the PL. The wavelengths of maximums corresponding to red luminescence bands characterizing the films $Ga_xAl_{1-x}P$ are presented in the same Table. It is seen from the Table that the red luminescence of substrate and films are at different wavelengths. The fact proves that the red PL observed in films characterizes the films $Ga_xAl_{1-x}P$.

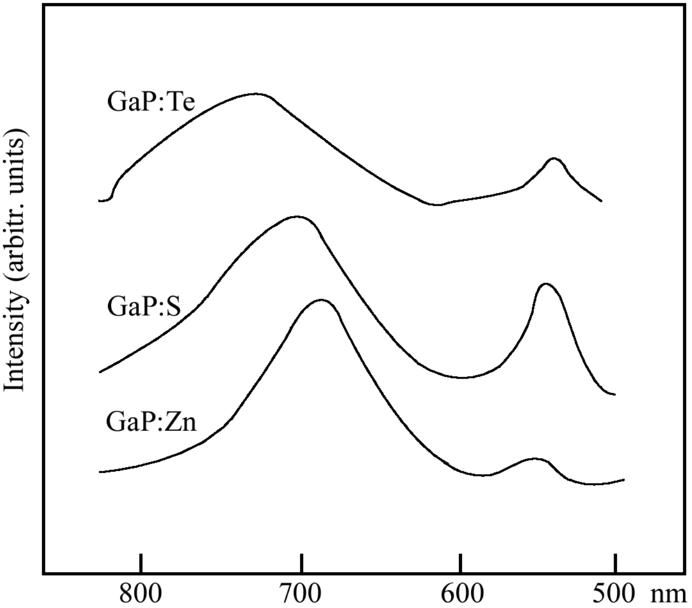

Fig.8. PL spectra with 488.0 nm excitation for zinc-, tellurium- and sulfur–doped GaP

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