PROPERTIES OF InP EPITAXIAL LAYERS DOPED BY RARE-EARTH ELEMENTS AND ALUMINUM[2]

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The influence of the complex doping by rare-earth elements (REE) (Yb and Sc) and Al on electro-physical and photoluminescent (at 10 K) properties of InP epitaxial layers obtained by liquid-phase epitaxy (LPE) is studied. It is established that, for the optimum ratios of Yb(Sc) and Al in the indium melt, the concentration of electrons in InP layers diminishes to (7×10^{13}—1×10^{14}) cm^{-3}, and the mobility achieves the values — 5000 cm^2/(V·s) (300 K) and (70000—74000) cm^2/(V·s) (77 K). The results of this experiment are explained by the gettering action of REEs in indium melts and by the influence of ytterbium on the redistribution of basic background admixtures over the sublattices of indium and arsenic.

1. Introduction

InP layers with low concentration of background admixtures and high mobility of electrons are used for making the solid-state detectors of high-energy particles [1] and also are introduced in the composition of multilayer heterostructures InP/InGaAs and InP/InGaAsP. On the basis of these heterostructures, p—i—n photodiodes [2] and light-emitting diodes in the range of waves 1.0—1.6 μm [3—4] are made.

The problem to derive the clean layers of InP is caused by the presence of background admixtures such as carbon, silicon, oxygen, manganese, and others in the components of charge, rigging, and technological gases [5].

The high-temperature annealing of a charge was used for cleaning from uncontrolled admixtures in the processes of LPE used in the environment of hydrogen cleared by a palladium filter [6]. Later, in work [7], the possibility to diminish the level of background admixtures in InGaAs layers by the addition of a small quantity of aluminum into the In melt was shown.

Today, one of the basic methods to derive clean uncompensated epitaxial layers is the doping of melts by REEs in the process of LPE. Minimum values of the concentration of electrons and the greatest values of the mobility in InP layers crystallized from In melts doped by Ho, Er, Nd, and Pr make (8×10^{14} — 3×10^{15}) cm^{-3} and 8000—16000 cm^2/(V·s) at 77 K [8—9], respectively. These values of electro-physical parameters are very far from the theoretically calculated limit for this material [10]. That is why, the search for the methods to derive high-quality materials which would allow one to achieve the high-quality cleaning of epitaxial layers from background admixtures and simultaneously to provide their high structural perfection in the scope of one technological process is the actual task.

From this viewpoint, a method which is based on the application of a complex doping by isovalent elements and REEs selected in optimum proportions is rather promising. For the first time, the efficiency of this method was shown in [11] at the derivation of uncompensated layers of GaAs, in which the concentration of electrons and their mobility at 77 K reached 1×10^{13} cm^{-3} and 48000 cm^2/(V·s), respectively.

The same approach to derive the uncompensated epitaxial layers of InP was applied by us in this work.

2. Experimental Technique

The epitaxial layers of InP were grown on semi-insulating (100) InP;Fe substrates by the LPE method in a graphite sliding boat from the indium (99.9999) melt.

The initial temperature of the epitaxy was 680 °C in the growth range covering 20 °C. The cooling rates were in the range 0.7—0.8 °C/min and were associated with supersaturations up to 10 °C. Aluminum, ytterbium, or scandium were added to the charge immediately before the loading into a quartz reactor tube. The concentration of Yb varied from 0 to 9.8×10^{-3} at%, Sc from 0 to 5.2×10^{-3} at.%, and Al from 0 to 4.5×10^{-2} at.% in the solution-melts. For the saturation of indium melts by phosphorus, we used polycrystalline InP with a concentration of free electrons of $(5\div7)\times10^{15}$ cm^{-3}.

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The homogenization of solution-melts took place during 1.5 h in the atmosphere of hydrogen, which was cleared by a palladium filter. The substrate InP:Fe was partly dissolved in the undersaturated indium melt before increasing the layer. The thickness of InP epitaxial layers was dependent on the growth period and was in the range 3—5 μm.

The low-temperature photoluminescence (PL) spectra were measured at a temperature of 10 K. The excitation was done by an Ar laser ($\lambda = 514.5$ μm) and a power of 200 mW/cm^2. Experimentally, we studied the dependence of the intensity of peaks of the exciton and admixture luminescences on the concentrations of Yb, Sc, and Al in the solution-melts of indium.

The concentration and mobility of charge carriers were measured at 300 and 77 K by using the Hall effect.

3. Results and Discussion

For the determination of the influence of the complex alloying by aluminum and REEs, such as Yb and Sc, on the properties of epitaxial layers of InP grew by the LPE method from In melt-solutions, several series of experiments were conducted. The purpose of these experiments was to establish the optimum ratios between Al and Yb or Sc in a melt, at which the concentration of majority carriers achieves a minimum, and the mobility of carriers reaches maximal values. "Complex alloying" means the simultaneous addition to a melt-solution of rare-earth and isovalent elements of the third and fifth groups. Moreover, the amount of an isovalent element is chosen to be such that the band gap width of the semiconductor is not changed, or this change is minimum and does not exceed 0.1 eV.

In the first series of experiments, we grew the layers of InP from the unalloyed melts of indium. The layers we have obtained had the n-type conductivity with a concentration of electrons of (6—7)$\times 10^{17}$ cm^{-3} and a mobility of 1500 cm^2/(V·s) at 300 K.

In the next series of experiments, the influence Sc and Yb on the electro-physical properties of InP layers obtained from indium melts was explored. These results are shown in Fig. 1,a,b. As seen in Fig. 1a, the addition of Sc and Yb to indium melts causes a reduction of the concentration of electrons in InP layers. For both admixtures, common is the inversion of the conductivity type in InP layers at their critical concentrations $N_{\rm cr}^{\rm Yb}$ and $N_{\rm cr}^{\rm Sc}$ in indium melt. The difference consists that, in layers of InP obtained from indium melts doped by scandium, the inversion takes place at lesser concentrations of Sc, than in the case of the doping by ytterbium.

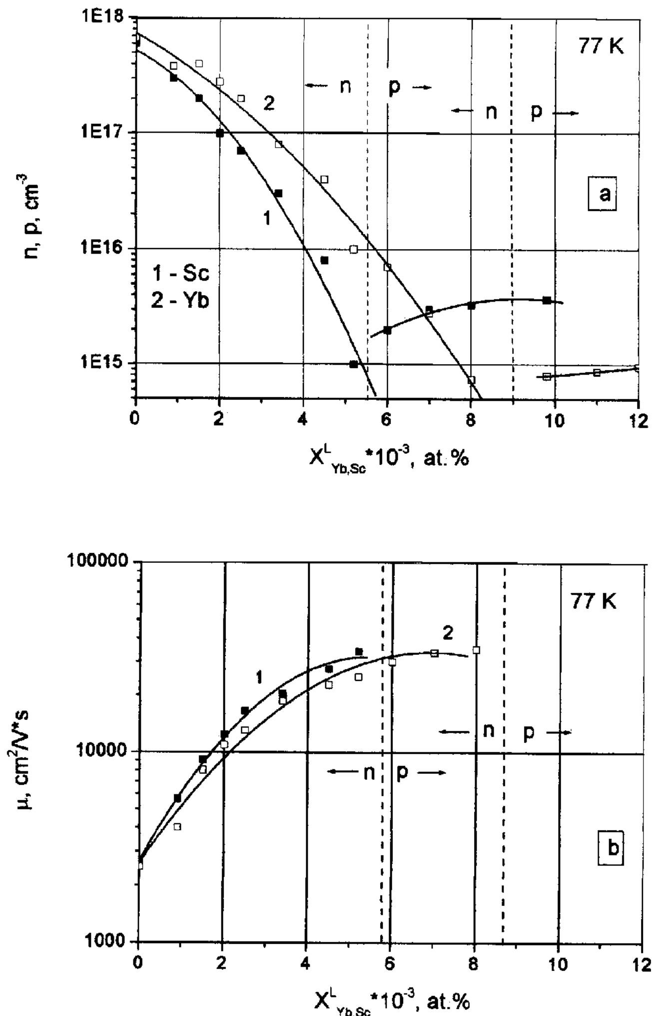

Fig. 1. Concentration of electrons (a) and their mobility (b) in the epitaxial InP layers versus Yb and Sc concentrations in the indium melt-solution

The reduction of the concentration of electrons in InP layers is accompanied by the increase of their mobility (Fig. 1,b), and its maximal value is achieved when the ytterbium and scandium concentrations in indium melts approach $N_{\rm cr}^{\rm Yb}$ and $N_{\rm cr}^{\rm Sc}$.

At the complex doping by Al and REEs of In melts, the pattern behaviour of the concentration and mobility of charge carriers in layers of InP (Fig. 2,a,b) is similar to that we look during the doping by only REEs. However, the comparison of the results shown in Figs. 1 and 2 evidences for some differences. The addition of Al in a melt causes a reduction of the critical concentrations

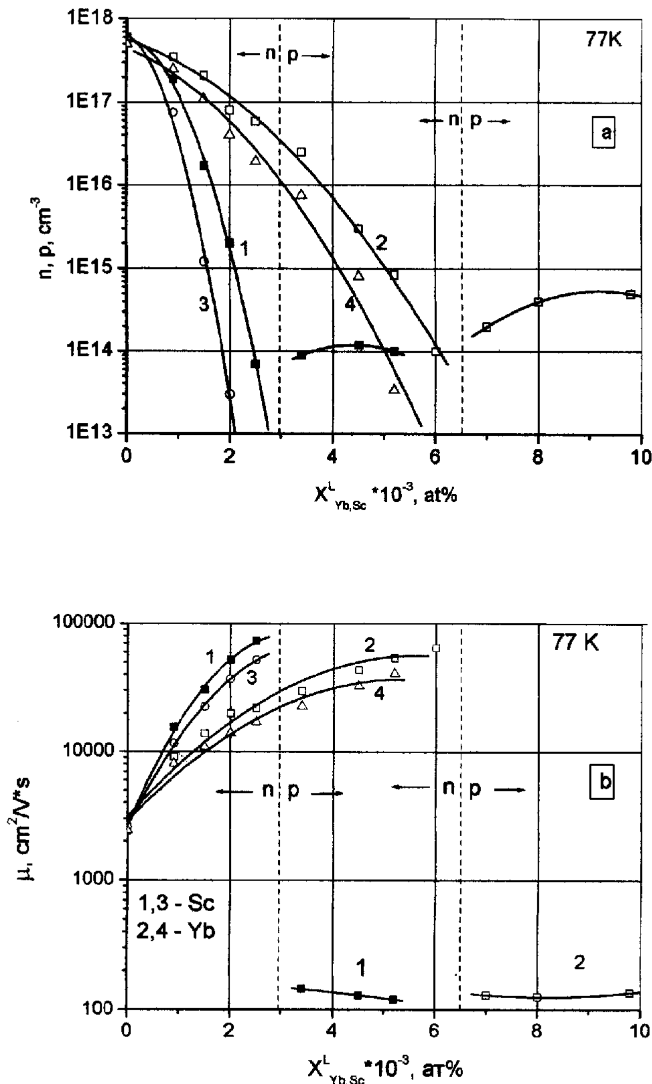

Fig. 2. Concentration of electrons (a) and their mobility (b) in the InP epitaxial layers versus Yb and Sc concentrations in the indium melt-solution at different concentrations of Al: *1, 2* — 1×10^{-3} at. %; *3, 4* — 3×10^{-3} at. %

$N_{\rm cr}^{\rm Yb}$ and $N_{\rm cr}^{\rm Sc}$ in the In melt, at which the conductivity type inversion takes place in layers of InP. The critical values of the concentrations $N_{\rm cr}^{\rm Yb}$ and $N_{\rm cr}^{\rm Sc}$ decrease with increase in the amount of Al added into the In melt (Fig. 2,*a,b*). At the complex doping, most sensible is the mobility of majority charge carriers. As we can see in Fig. 2,*b* (curves *1* and curves *2*) and Fig. 1,*b* (curves *1* and *2*), the mobility in layers of InP under the complex doping by Yb (Sc) and Al (1×10^{-3} at.%) achieves the values of (60000—70000) cm^2/(V· s) at 77 K. In the layers doped only by ytterbium or scandium, this value does not exceed 25000 cm^2/(V· s) at 77 K. Our studies

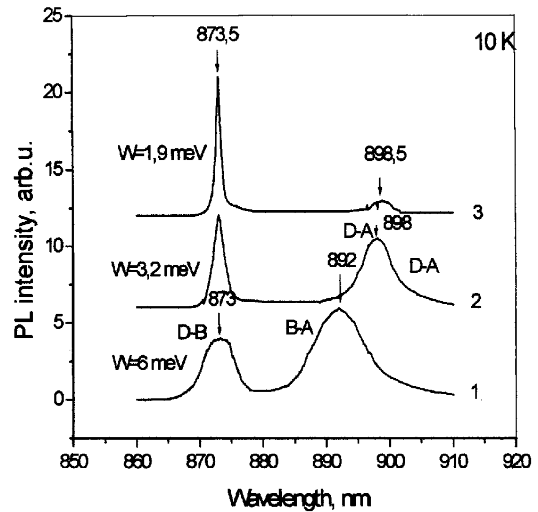

Fig. 3. PL spectra of InP epitaxial layers obtained by the LPE method from In melts which were measured at 10 K: *1* — InP epitaxial layers obtained from In melts; *2* — InP epitaxial layers obtained from In melts doped by Yb (5.2×10^{-3} at. %); *3* — InP epitaxial layers obtained from In melts doped by Yb(5.2×10^{-3} at. %) + Al(1×10^{-3} at. %)

showed that the mobility of electrons achieves the maximal values at a concentration of Al of 1×10^{-3} at.%. The increase in the amount of Al by 1.5—2 times above the indicated value results in a reduction of the mobility of carriers, though it is accompanied by some reduction of their concentration (Fig. 2,*a*, curve *3* and *4*).

Low-temperature PL spectra (10 K) of the unalloyed samples of InP (curve *1*) doped by Yb in the optimum concentration (curve *2*) and complexly doped by Yb+Al (curve *3*) are shown in Fig. 2. Two bands are present in the spectra of the unalloyed samples of InP with a concentration of carriers $(5—6)\times10^{17}$cm^{-3}. The first one $(D-B)$ with a maximum at 873 nm is conditioned by the transitions of electrons from donor levels into the valence zone, and the second band $(B-A)$ with a maximum at 892 nm is caused by the band-acceptor transitions of electrons.

There are also two bands in the spectra of epitaxial layers of InP doped by Yb in the optimum concentration $(5—6)\times10^{-3}$ at.% (see curve *2*) and complexly doped by Yb $(5—6)\times10^{-3}$ at.% + Al (1×10^{-3} at.%) (see curve *3*) in the optimum concentrations. Near the band edge, the exciton band with a maximum at 873.5 nm and the band conditioned by the recombination of donor-acceptor pairs $(D-A)$ with a maximum at 898.5 nm dominate. The intensity of the $(D-A)$ band in the spectra of the samples obtained from indium melts by the complex doping by Yb and Al is insignificant.

In the PL spectra of the epitaxial layer doped by Yb (Fig. 2, curve *3*), a band with a maximum at 873 nm prevails. It is related to the free-exciton annihilation [12]. The half-width of this band diminishes with increase in the concentration of Yb in the indium melt and take 6 meV at its optimum concentration. A similar effect was observed in works [13—14] in epitaxial layers of InP doped by REEs Nd, Ho, and Tb. In the epitaxial layers of InP obtained from indium melt-solutions doped by Yb and Al in the optimum concentrations (Fig. 3, curve *3*), the intensity of the exciton band with a maximum at 873.5 nm is greater, and its half-width diminishes almost by twice in comparison to its value in the layers doped by Yb only. At the same time, the band caused by the recombination of donor-axceptor pairs with a maximum at 898.5 nm almost fully goes out, even in comparison to a sample doped by ytterbium in the optimum concentration. Thus, for samples doped by ytterbium (Fig. 3, curve *2*) and for those doped by Yb and Al in the optimum concentrations (Fig. 3, curve *3*), the shift of the band caused by the transition $(D-A)$ in the long-wave part of the spectrum relative to its initial position with a maximum at 892 nm (Fig. 3, curve *1*) is observed.

The reduction of the concentration of electrons and the conductivity type inversion, which take place at the critical concentrations of REEs in melts, can testify to a decrease of the concentration of donor centers or the addition of additional acceptor centers into layers of InP at the complex doping of indium melts. Scandium and ytterbium, as well as aluminum, are elements of the third group. They cannot be such acceptors in InP, which would compensate the donor centers present in it. The high mobility of electrons (60000—70000)$\mathrm{cm}^2/(\mathrm{V}\cdot\mathrm{s})$ in layers grown from indium melts doped by Al and Sc and Yb testifies to a low degree of indemnification (Fig. 2). That‘s why, the acceptor action of REEs can be caused by the restriction of the access of uncontrolled admixtures to an epitaxial layer which is crystallized.

It is well known that silicon, oxygen, and sulphur are basic background admixtures in InP [5]. There exist at least two mechanisms which would describe the processes of clearing of InP epitaxial layers. The first one consists in that scandium and ytterbium can occupy vacant sites in the sublattice of indium and, at the same time, can decrease the probability of the entrance of uncontrolled donor admixtures in the epitaxial layer. The covalent radii of atoms of scandium and ytterbium (1.44 and 1.57 Å, respectively [15]) are close to the covalent radius of indium, 1.50 Å. However, the probability of the entrance of these elements into the indium sublattice is low, because of the insignificant solubility of REEs in epitaxial layers of InP [16]. The second mechanism proves that REEs interact with background admixtures, oxygen, sulphur, and silicon, in indium melts with the formation of compounds which remain in the melt during the crystallization of the epitaxial layer. The probability for this mechanism to realize is high enough, taking into account the fact that a number of binary and triple compounds arise [17] in binary (REE—O_2, REE—Si, REE—S) and triple systems (REE—In—O2, REE—Al—O_2, RZE—Al—Si). Such an explanation is supported by the experimental data which indicate that the mobility of electrons near the point of inversion is higher in the layers doped by scandium (Fig 2,*b*, curve *1*) than in those doped by ytterbium, because the chemical activity of scandium higher than that of ytterbium.

Consider the complex doping by aluminum and ytterbium. Since the covalent radius of Al is close to that of indium, it can partly fill the vacant sites of the indium sublattice and can also interact in the melt with some background admixtures (oxygen, sulphur) preventing their entrance into the crystalline lattice of epitaxial layers of InP in the process of crystallization. This results in the enhancement of the structural perfection of layers and in a more substantial reduction of the concentration of uncontrolled admixtures. This assertion is confirmed by the increase of both the mobility of majority charge carriers and the intensity of the exciton band with a maximum at 873.5 nm and by the almost full decay of the band with a maximum at 898.5 nm (Fig. 3, curve *3*), the latter band being caused by donor-acceptor transitions.

The shift of the band with a maximum at 892 nm to the long-wave part of the spectrum can be explained by the presence of the great variety of donor and acceptor background admixtures in indium melt-solutions and by the different efficiencies of the interaction of these admixtures with REEs, aluminum, and indium.

The band with a maximum at 898 nm is caused by donor-acceptor transitions of type *a* in Fig. 4. Today, there is no unique interpretation of the nature of donors and acceptors responsible for these transitions [12, 14].

It is possible to examine two variants of the processes which are responsible for the shift of the band with a maximum at 892 nm to the long-wave region up to 898.5 nm. According to the first variant, the introduction of Yb into the melt causes the binding of donors of mainly one sort, for example D_1. Other donors interact with Yb less effectively. At certain concentrations of Yb in melts, the concentration of donors of the type D_1 becomes

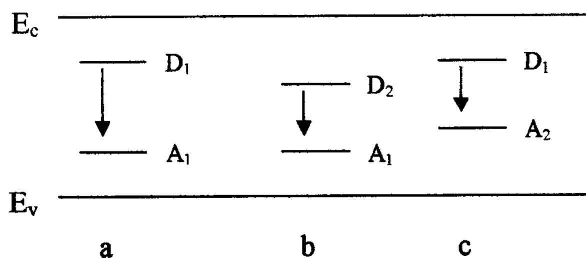

Fig. 4. Most probable processes of transition of electrons in the band-gap of InP that can be responsible for the displacement of the peak with a maximum at 892 nm in PL spectra of InP epitaxial layers doped by Yb and Al

comparable with that of donors of the other type, D_2. Therefore, the band with a maximum at 898 nm which is caused by transitions of type *b* (Fig. 4) begins to dominate in the PL spectrum rather than that at 892 nm.

According to the second variant, transitions of type *c* (Fig. 4) in the layers begin to prevail as a result of action of Yb. Due to a reduction of the donor background, the transitions of electrons on acceptor levels A_2 become dominant if the concentration of acceptor centers A_2 is much smaller than A_1 (Fig. 4). Thus, the energy of transitions D_2—A_1 and D_1—A_2 are approximately identical. It should be noted that donors or electric active centers such that a reduction of their concentration leads to a decrease in the concentration of majority charge carriers (Figs. 1,2) not necessarily give a contribution to the band with a maximum at 892 or 898 nm. These donors can be quite different by their nature. The determination of the probability of each considered process needs additional studies.

The clearing mechanism upon the complex doping has a complicated character and connects the chemical interaction of REEs with In and background admixtures with the formation of chemical compounds, as well as the interaction and redistribution of point defects under the action of an isovalent admixture, aluminum. The efficiency of such a clearing upon the complex doping is considerably higher than in the case of the application only of REEs.

4. Conclusions

It is established that, upon the complex doping of indium melts by Yb and Al, the concentration of electrons in epitaxial layers of InP diminishes to 1×10^{14} cm $^{-3}$, and the mobility achieves the values 4900 cm^2/(V·s) (300 K) and 65000 cm^2/(V·s) (77 K). For the optimum ratios of Sc and Al in the melts, the concentration of electrons in InP layers diminishes to 7×10^{13} cm $^{-3}$, and the mobility increases and becomes equal to 5000 cm^2/(V·s) (300 K) and 74000 cm^2/(V·s) (77 K).

Thus, it is shown that, for the InP epitaxial layers grown from In melts like the case of GaAs obtained by the LPE method from gallium melts [11], the complex doping of In melts by rare-earth and isovalent elements in the optimum concentrations causes a considerable enhancement of both the structural perfection of InP layers and the effect of their clearing from background admixtures.

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ВЛАСТИВОСТІ ЕПІТАКСІЙНИХ ШАРІВ InP, ЛЕГОВАНИХ РІДКІСНОЗЕМЕЛЬНИМИ ЕЛЕМЕНТАМИ ТА АЛЮМІНІЄМ

С.І. Круковський, Й.М. Стахіра, В.Д. Фотій

Р е з ю м е

Досліджено вплив комплексного легування рідкісноземельними елементами (Yb і Sc) та Al на електрофізичні та фотолюмінесцентні властивості епітаксійних шарів InP, отриманих методом рідкофазної епітаксії. Встановлено, що для оптимальних співвідношень Yb(Sc) та Al в розплаві індію концентрація електронів в шарах InP зменшується до $7{\cdot}10^{13}$ — $1{\cdot}10^{14}$ см$^{-3}$, а рухливість досягає значень 5000 см^2/(В·с) при 300 К і 70000—74000 см^2/(В·с) при 77 К. Отримані результати пояснюються гетерувальною дією рідкісноземельних елементів у розплаві індію, а також впливом ітербію та алюмінію на перерозподіл основних фонових домішок по підрешітках індію та миш'яку.