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Influence of Yb AND Yb_2O_3 addition on the properties of InP layers

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The influence of Yb and Yb_2O_3 additions into the LPE growth melt on the properties of InP epitaxial layers is reported. We have concentrated on the investigation of gettering and/or doping effects. Efficient gettering was confirmed for both Yb and Yb_2O_3 addition, the incorporation of Yb^{3+} into the InP lattice was confirmed only for Yb addition. Layers grown with Yb addition exhibited *n→p* conductivity conversion at certain Yb concentration. Dominant acceptor, responsible for *n→p* conductivity conversion was identified as the isoelectronic Yb impurity on the In site. Layers grown with Yb_2O_3 admixture always show *n*-type electrical conductivity.

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1. Introduction

The exceptional behaviour of rare earth (RE) elements has two aspects for feasible employment in semiconductor technology. Firstly, the 4f electrons of RE atoms are to a considerable degree shielded from external influences. If the RE atom or ion is inserted into a host lattice, the spin-orbit interaction and the crystal field cause splitting of 4f levels, which gives rise to the possibility of intra-centre transitions corresponding to near- and mid-infrared frequencies, independent of the host, that are of interest for producing temperature stable radiation sources [1]. Secondly, REs exhibit considerable chemical reactivity and reduction capability that can be exploited in technological processes. It has been shown that REs can act as very efficient purification agents in removing undesirable residual impurities during the growth of semiconductor epitaxial layers [2].

In recent years, we have pursued the investigation of the influence of the admixture of RE in the growth melt on electrical and luminescence properties of InP epitaxial layers [3]. It has been shown that the admixture of Ce, Pr, Tb, Dy, Yb, Tm, Eu, Tm_2O_3, and Eu_2O_3 leads, at certain concentrations, to the reversal of InP conductivity type from *n* to *p*. Out of these admixtures, only Yb and Ce have been incorporated into the InP lattice in our laboratory. The possibility to use RE elements and oxides as efficient gettering agents to prepare pure and thick InP epitaxial layers for radiation detection has been pointed out recently [3]. In particular it has been shown that the possibility to prepare layers of p-type electrical conductivity without intentional doping is of great advantage in the context of radiation detectors.

The purpose of this contribution is to describe the preparation of InP epitaxial layers with the addition of Yb and Yb_2O_3 into the growth melt and to compare their influence on the layer properties. In particular to confirm preliminary indications that Yb ions are not incorporated into the InP lattice when Yb_2O_3 is added to the growth melt.

2. Experimental

Single crystal InP layers were grown on (100) oriented *n*-type InP:Sn or on semi-insulating (SI) InP:Fe substrates by LPE from the melt containing besides basic components also Yb in the forms of metal and oxide. Their concentrations varied within 0.001 – 0.1 at% while the basic composition of the melt remained fixed. The whole process was performed in a quartz reactor tube with a graphite boat under Pd-purified hydrogen atmosphere at the initial temperature in the range 650 – 630 ºC. The In melt was prebaked at 900 °C for 24 hrs to reduce the residual impurities. After the baking process the system was cooled to room temperature and the cleaned InP substrate and growth components with RE admixture were loaded into the boat. A proximity cap InP wafer was used to prevent phosphorus evaporation from the substrate prior to the epitaxy. The apparatus was heated up to 700 ºC, kept at this temperature for 60 min and then cooled down to the growth temperature where supercooled growth was initiated. Some details of the technology were described elsewhere [4]. The surface morphology, the structural defects, and the layer thickness were evaluated by optical and scanning electron microscopy. The chemical composition and depth chemical profile were traced by Secondary Ion Mass Spectroscopy (SIMS). Electrical and optical properties were assessed by the capacitance-voltage (C-V) and temperature dependent Hall measurements together with low temperature photoluminescence (PL) spectroscopy. The estimates of impurity concentrations on the samples without contacts were gained from C-V measurements performed with a mercury probe. More substantial were results obtained on

the base of the temperature dependent Hall Effect on contacted layers grown on SI InP substrates. PL spectra were taken at various temperatures and excitation levels and were analyzed by 1 m focal length monochromator coupled with a cooled Ge detection system or cooled GaAs photomultiplier.

3. Results and discussion

It has been shown [4] that the morphology and the defect density of epitaxial layers prepared with the addition of RE elements reflect the concentration of RE added to the melt. Structural defect sites and inhomogeneities were revealed by several chemical etchants and monitored in order to trace the influence of Yb and Yb_2O_3 addition as a function of their concentration. Typically, Yb concentration below 0.02 at% resulted in sufficiently smooth surface with the reduction of structural defect density by a half order of magnitude with respect to the layers grown without Yb admixture. However, when the concentration exceeds the limit of 0.02 at%, defect sites appear on the surface; the defect density is considerably increased. Oxide is not as reactive as an element, so precipitate nodules incorporate into the InP layer for Yb_2O_3 concentrations exceeding 0.1 at%. Thus, the limiting concentrations mentioned above differ for Yb and Yb_2O_3 though the overall trend is similar. Typical layer thickness was in the range 12 – 14 μm. The layer thickness exhibited dependence on the growth period and on the supercooling regime. The presence of Yb or Yb_2O_3 in the growth melt did not lead to the decrease of the growth rate.

Table 1. Summary of technological and electrical parameters of epitaxial layers grown with the admixture of Yb and Yb_2O_3.

Sample	RE concentrations and relevant electrical parameters		
	RE concentration (10^{-2} at%)	*Conduction type*	*Donor/accept or concentration (cm^{-3})*
InP	0	*N*	3.7×10^{17}
InP(Yb)	0.3	*N*	8.7×10^{14}
InP(Yb)	0.6	*N*	2.8×10^{14}
InP(Yb)	1.2	*P*	1.3×10^{16}
InP(Yb_2O_3)	2.5	*N*	4.2×10^{16}
InP(Yb_2O_3)	5.1	*N*	2.0×10^{16}
InP(Yb_2O_3)	7.8	*N*	2.4×10^{15}

The dependence of conduction type and donor/acceptor concentration on RE admixture was determined by Hall Effect and C-V measurements. Relevant electrical parameters of selected InP layers with Yb and Yb_2O_3 concentrations in the melt are given in Table 1.

The addition of Yb leads to a pronounced reduction of undesirable electrically active impurities by up to three orders of magnitude. Higher Yb concentration leads to the change of electrical conductivity from *n*- to *p*- type and thus layers prepared with Yb addition exhibit both *n*- and *p*- conductivity types.

Typical temperature dependences of the hole concentration and mobility for *p*-type InP layers doped with Yb are shown in Fig. 1. For comparison are also shown the corresponding data for InP grown with Ce and for single crystal InP doped with Zn, which has a binding energy 43 meV. The curves for *p* concentration reveal a straight line at low temperatures giving the binding energy (after the $T^{3/2}$ correction) of the dominant acceptor equal to 37 meV and 31 meV for Yb and Ce addition, respectively. It could be seen from Fig. 1 that layers prepared with Yb and Ce addition exhibit fairly similar temperature dependences of both the hole concentration and mobility. Comparison with samples doped with Zn is included to demonstrate that $n \rightarrow p$ conductivity conversion is not due to residual Zn impurity. Data for samples grown with the admixture of Ce are plotted to show similar electrical behavior of those RE ions that have been successfully incorporated into the InP lattice. The energy level schemes of 4f shells of both Ce and Yb are relatively simple with only one excited state. While Ce^{3+} ion is characterized by one 4f electron, the Yb^{3+}ion has thirteen 4f electrons, thus the two elements have a somewhat complementary position within lanthanide series.

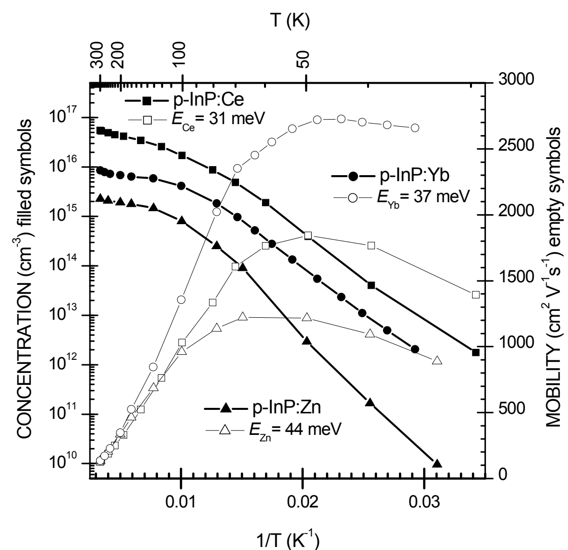

Fig. 1. Hole concentration and mobility of InP grown with Yb addition (circles). For comparison are also shown the same data for single crystal InP doped with Zn and InP grown with Ce addition.

Temperature dependent Hall measurements of *p-type* InP layers grown with Ce and Yb admixtures have been performed from room temperature to about 35 K [3, 5]. Below this threshold temperature, the conductivity of samples changes very slowly, so the temperature equilibrium cannot be reached within hours. A slow decay

of the conductivity starts to be observed at about 60 K. When the temperature of samples is stabilised within 0.05 K, the decays of conductivity lasting from minutes at 60 K to an hour at 35 K are monitored. Thus, InP layers grown with the addition of Yb and Ce approach a metastable state at temperatures below 35 K and results of Hall measurements are not reliable any more. Yb and Ce are subjected to a strong electron-lattice interaction due to their much larger atomic radii as compared to that of In and due to the large difference between electronegativities of Yb, Ce and In. A potential barrier raised by this interaction is believed to be responsible for the observed metastability of the electrical conductivity.

It has been concluded [5] that dominant acceptors responsible for the conductivity conversion from *n→p* in InP:Yb layers are Yb^{3+} ions incorporated into the InP lattice. The Yb impurity in InP is known [6] to be incorporated as a cubic Yb^{3+} centre on the cation site (In).

Layers prepared with Yb_2O_3 addition were always of *n*- type conductivity. Yb_2O_3 addition leads to a reduction of impurities by up to two orders of magnitude and does not lead to the change of the electrical conductivity, in the investigated range of Yb_2O_3 concentrations added to the melt.

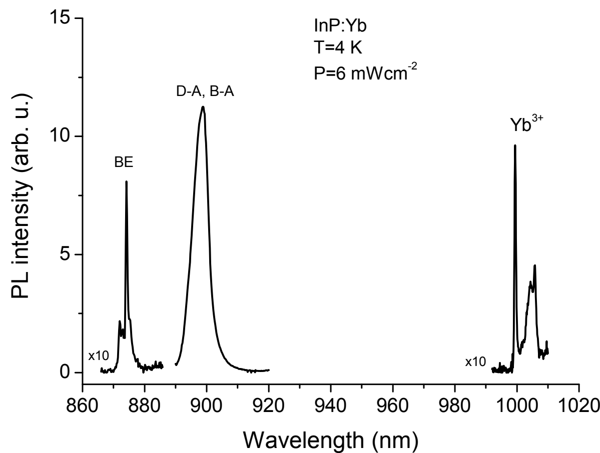

Fig. 2. Low temperature luminescence of InP grown with Yb addition.

Low temperature PL spectra of samples doped with Yb were measured for different excitation power densities (6 – 600 mW cm^{-2}) and temperatures (4 – 300 K). Typical low-temperature PL spectra of InP layers grown with the admixture of Yb and Yb_2O_3 are shown in Fig. 2 and Fig. 3, respectively. The observed radiative transitions in InP could be grouped into three categories: band-edge (BE) transitions at about 874 nm (1.418 eV), shallow impurity related transitions (D-A, B-A) at 898 nm (1.38 eV), and deep-level transitions at 1087 nm (1.14 eV) due to Mn [3]. The major manifestation of Yb and Yb_2O_3 additions is a considerable narrowing of the PL spectra and the corresponding appearance of fine spectral features, characteristic of pure material. The sharp 4f-4f radiative transitions resulting from inner shells of Yb^{3+} ions were detected at 1000 nm in PL spectra of InP layers grown with Yb. This observation gives a direct proof of Yb incorporation into the InP lattice.

PL spectra measured on InP layers prepared with the addition of Yb_2O_3 did not show 4f-4f transitions (Fig. 3), so Yb_2O_3 is assumed to act as a purification agent only. The energy level scheme of Yb^{3+} ion enables only one 4f-4f transition, $^2F_{5/2}\rightarrow{}^2F_{7/2}$, at 1000 nm. No luminescence has been found in this range on samples prepared with Yb_2O_3 admixture even at elevated excitation intensity. At the elevated excitation intensity we could only detect -2LO phonon replica of shallow acceptor related level at 957 nm and a broad band due to Mn impurity with a no-phonon (NP) line at 1042 nm.

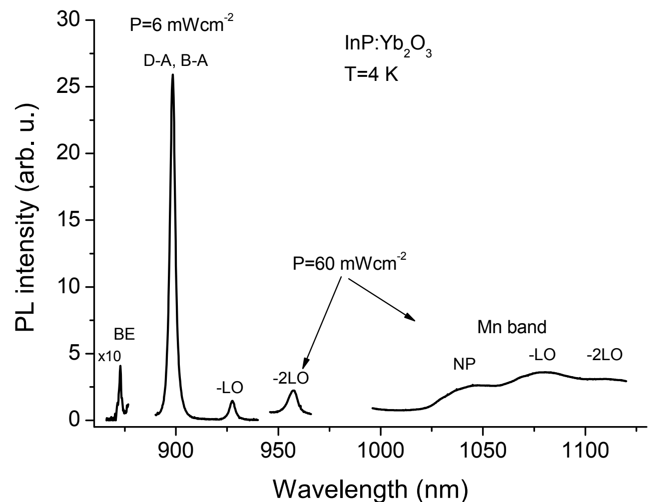

Fig. 3. Low temperature luminescence of InP grown with Yb_2O_3 admixture.

As stated above, in the case of Yb addition, the change of electrical conductivity type from *n→p* has been observed at about 0.6×10^{-2} at. % of Yb in the melt, and the characteristic 4f-4f inner shell transitions of Yb^{3+} ions have been observed on both *n* and *p*-type epitaxial layers. We conclude that the absence of 4f-4f radiative transition in PL spectra of the layers grown with Yb_2O_3 admixture reflects the fact that Yb ions are not incorporated into the InP lattice, which seems to be in accord with a higher tendency of Yb_2O_3 to create complex compounds with phosphorus as compared to Yb admixture in the form of metal. This conclusion is further supported by the fact that the *n→p* conductivity conversion does not take place in this case. Thus, the purification due to Yb_2O_3 addition does not seem to be efficient enough to secure the conductivity conversion due to the preferential RE gettering of residual *n*-type impurities. We can suggest that the presence of chemically free Yb atoms in the melt is a prerequisite for Yb incorporation into the InP lattice.

The chemical composition of prepared layers has been evaluated by Secondary Ion Mass Spectroscopy (SIMS). The depth chemical profile of InP grown with Yb addition is shown in Fig. 4. The composition dependence on the depth confirms the incorporation of Yb into the InP lattice.

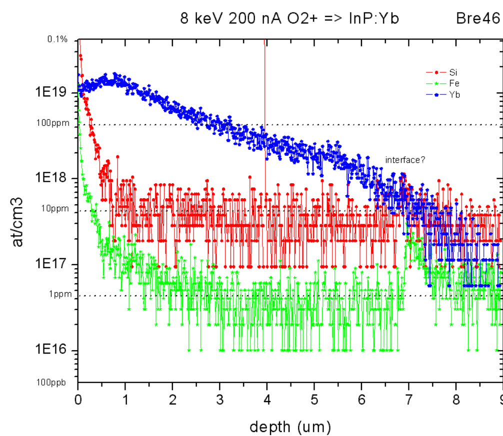

Fig. 4. The SIMS depth profile of InP layer grown with the addition of Yb.

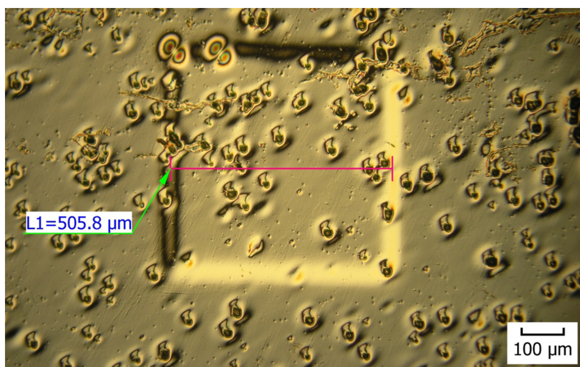

Fig. 5. Optical micrograph of etched InP layer surface.

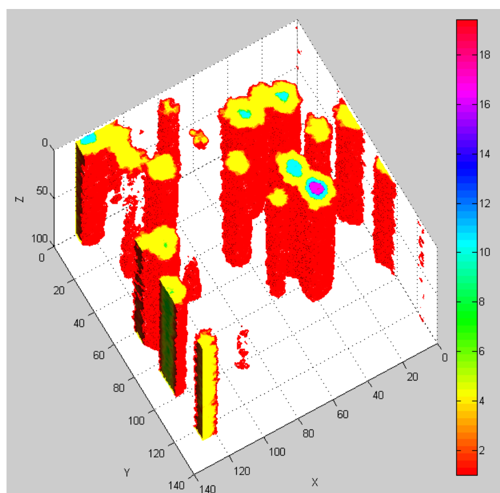

Fig. 6. 3D-SIMS map of the profile of the chemical composition for Yb in the crater.

The studies of SIMS depth concentration profile were performed on etched surfaces of InP:(Yb) layers. The layer surface etched by H_2SO_4:H_2O_2:H_2O is shown in Fig. 5. The crater width was about 500 µm. Fig. 6 shows a 3D SIMS map of the chemical composition in the crater for Yb. The scale of the x and y axes corresponds to 500 µm and the scale of the z axis corresponds to 1.35 µm.

4. Conclusions

Both Yb and Yb_2O_3 act as efficient purification agents when added to the melt during LPE growth of InP layers. Layers grown with the addition of Yb exhibit *n→p* conductivity conversion, while layers prepared with Yb_2O_3 admixture are always of *n-type* electrical conductivity. It has been confirmed that the admixture of Yb leads to the incorporation of Yb^{3+} ions into the grown epitaxial layers while the admixture of Yb_2O_3 does not. The incorporation of Yb into the grown layers is supported by the temperature dependent Hall measurements, low temperature PL, and SIMS depth-profiles. It follows from the temperature dependent Hall measurements that the dominant acceptor impurity responsible for *n→p* conductivity change has a binding energy of 37 meV and exhibits a slow decay of conductivity for temperatures below 60 K. We identified this dominant acceptor impurity as Yb introduced into the InP lattice in the form of isoelectronic impurity in the In site. Inner shell 4f-4f radiative transitions of Yb^{3+} ions have been observed by PL spectroscopy as a direct proof of Yb incorporation into the lattice. In addition, Yb has been detected in the SIMS depth profiles to the depth of 7 µm below the layer surface, which corresponds well with the layer thickness. No evidence of the Yb incorporation into epitaxial layers grown with the admixture of Yb_2O_3 has been found.

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