

EPITAXIAL LAYERS OF InP DOPED WITH RARE ELEMENTS FOR USE IN RADIATION DETECTOR.

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Summary We have focused on the investigation of the impact of Ce, Eu, Tm, Eu₂O₃ and Tm₂O₃ addition in LPE growth process on the properties of InP layers in the context of their application in detector structures.

1. INTRODUCTION

High quality InP-based semiconductors, both bulks and thick epitaxial layers, are promising materials for the preparation of room temperature radiation detectors for energy range 10-500 keV [1, 2]. In the context of radiation detection the preparation of Schottky-type blocking contacts would be of great advantage for good performance of detectors. At present state of the art, Schottky contacts on *p-type* InP can be made with a large barrier height and low leakage current which cannot be reached on *n-type* InP. Thus preparation of *p-type* semi-insulating (SI) InP bulks or thick *p-type* InP epitaxial layers is of great importance.

Liquid Phase Epitaxy (LPE) technique allows growing of thick and structurally perfect layers. In our laboratory an effort has been devoted to the optimization of the LPE growth by utilizing the admixture of rare earth (RE) elements in the growth melt [3,4]. We were particularly interested in the preparation of relatively thick (>10 μm) layers that are structurally perfect, free of defects and with residual impurity concentration below 10¹⁵ cm⁻³.

2. EXPERIMENTAL

Single crystal layers of InP were grown on the (100) InP:Sn or on semi-insulating (SI) InP:Fe substrates by LPE technique. In reported experiments RE elements were used in the form of metals (Ce, Tm, Tb and Dy) or oxides (Tm₂O₃ and Eu₂O₃). Their concentrations in the growth melt varied within 0.008 - 1.4 at%. Typical layer thickness was about 10 μm. Details of the technology are described elsewhere [3].

Characterization of structural, electrical and optical properties was performed by employing the microscopy, capacitance-voltage (C-V) and temperature dependent Hall effect measurements together with low temperature photoluminescence (PL) spectroscopy. Electrical properties were assessed via the capacitance-voltage (C-V) and temperature dependent Hall effect measurements.

The wafers of InP were prepared for characterization by galvanic-magnetic measurements. Four small area In contacts furnished with thin wires were made for the resistivity and Hall coefficient measurements in the van der Pauw configuration. InP crystals were characterized by measurements of resistivity ρ and Hall coefficient R_H . The measurements were performed on the computer controlled equipment with high-impedance inputs and a switchbox for alternate engaging of various contacts during the measurement. Software for finding electrically stabilized states and averaging the measured values of current and voltage was built up to minimize experimental errors. The samples were placed in vacuum ambient either in the closed cycle helium cryostat enabling temperature variation from 6.5 K to 320 K or in the liquid N₂ cryostat for temperatures from 80 K to 430 K. The thermal supply to a sample was provided through a copper extender encroaching into the magnetic field. Sample plates were stuck to the extender by Silicon Heat Sink Compound paste through a piece of kapton foil furnishing good heat contact and electrical insulation.

The estimates of the impurity concentrations on samples without contacts were gained from C-V measurements performed with the mercury probe. More substantial were measurements of the temperature-dependent Hall effect on contacted samples in the van der Pauw configuration.

Photoluminescence spectrometer equipped with the He closed cycle refrigerator system enables measurements in the temperature range 3.5 -300K and spectral range 300 – 5000 nm.

3. RESULTS AND DISCUSSION

Structural properties of grown InP layers reflect the concentration of RE elements or RE oxides added to the melt. Typically, RE concentrations below 0.2 at% resulted in the reduction of structural defect density by a half order of magnitude with respect to layers grown without RE admixture. However, when the RE concentration in the melt exceeds the limit of 0.2 at%, the structural defect density is increased considerably, with many defect

sites on the surface. Though the overall trend is similar, the limiting concentrations given above, may differ for individual RE.

The admixture of oxides Tm_2O_3 and Eu_2O_3 does not follow the rules mentioned above. The surface morphology was sufficiently smooth with very few defect sites up to concentrations around 0.7 at%. Oxides are not as reactive as elemental RE so that precipitate nodules incorporate into the InP layer for oxide concentrations exceeding 1.4 at%. Structural defects were revealed by using several chemical etchants.

Some electrical parameters of selected InP layers with RE element or RE oxide concentrations added to the melt are listed in Table 1 for Ce, Tm, Tm_2O_3 , Eu_2O_3 and Eu_2O_3+Tb or Dy.

Table 1. Relevant electrical parameters and RE concentrations in the melt for selected InP layers.

Sample	RE content, (at%)	Type	N_d/N_a , (cm^{-3})
InP	0	<i>n</i>	$4.8 \cdot 10^{17}$
InP (Ce)	$9.4 \cdot 10^{-5}$	<i>p</i>	$1.6 \cdot 10^{17}$
InP (Ce)	0.34	<i>p</i>	$2.0 \cdot 10^{17}$
InP (Ce)	0.15	<i>p</i>	$5.5 \cdot 10^{16}$ **
InP	0	<i>n</i>	$8.9 \cdot 10^{17}$
InP (Tm)	$8.0 \cdot 10^{-5}$	<i>n</i>	$2.9 \cdot 10^{16}$ *
InP (Tm)	$6.6 \cdot 10^{-2}$	<i>p</i>	$2.5 \cdot 10^{15}$ *
InP (Tm)	$5.4 \cdot 10^{-2}$	<i>p</i>	$7.4 \cdot 10^{14}$ *
InP	0	<i>n</i>	$8.9 \cdot 10^{17}$
InP (Tm_2O_3)	$2.6 \cdot 10^{-2}$	<i>n</i>	$8.4 \cdot 10^{17}$ *
InP (Tm_2O_3)	0.69	<i>p</i>	$1.5 \cdot 10^{15}$ **
InP (Tm_2O_3)	1.42	<i>p</i>	$2.9 \cdot 10^{15}$ *
InP	0	<i>n</i>	$9.6 \cdot 10^{17}$ *
InP (Eu_2O_3)	0.14	<i>n</i>	$2.5 \cdot 10^{14}$ *
InP (Eu_2O_3)	0.23	<i>p</i>	$2.6 \cdot 10^{15}$ *
InP (Eu_2O_3)	4.1	<i>p</i>	$3.2 \cdot 10^{15}$ *
InP(Eu_2O_3+Tb)	$0.14+4.9 \cdot 10^{-2}$	<i>p</i>	$3.6 \cdot 10^{15}$ **
InP(Eu_2O_3+Dy)	$0.14+6.8 \cdot 10^{-2}$	<i>p</i>	$8.1 \cdot 10^{15}$ **

N_d/N_a — donor/acceptor concentration

* deduced from C-V curve at 300 K using Hg probe

** deduced from Hall measurement at 77 K

Layers prepared with Ce addition were of *p-type* conductivity and layers prepared with Tm, Tm_2O_3 , Eu_2O_3 and co-admixture of Eu_2O_3 with Tb and Dy were of both *n* and *p-type* conductivity types. Layers grown with the addition of Tm on InP:Fe semi-insulating substrates were found to be converted to SI state, even for very small Tm concentrations. High purifying effect has been obtained with Tm_2O_3 and Eu_2O_3 additions, where the impurity concentrations were decreased by three orders of magnitude, while only one order of magnitude decrease was observed in the case of Ce addition.

Layers of *p-type* conductivity grown on SI substrates were further analysed by the temperature dependent Hall measurements in order to identify

the dominant impurity responsible for observed *n*—*p* conductivity change. Even samples grown with very small Ce admixture appear to be of *p-type* conductivity. This suggests that Ce itself is the impurity responsible for conductivity crossover.

Hole concentration and mobility for InP layers grown with the admixture of Ce are shown in Fig. 1 together with corresponding data on samples prepared with Yb addition. Data measured on bulk InP:Zn crystals are shown in Fig. 1 for comparison.

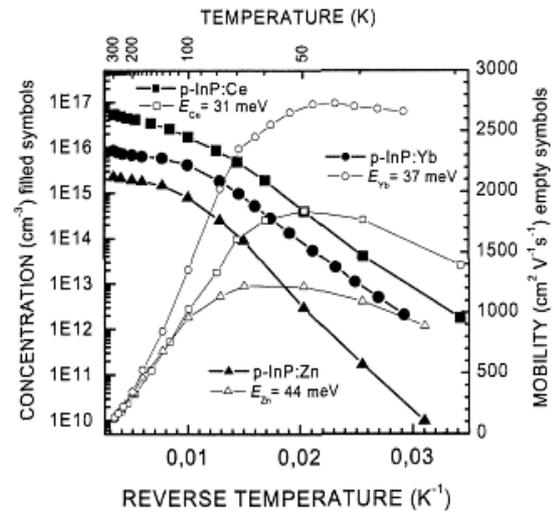


Fig. 1. Hole concentration and mobility for InP layers grown with Yb and with Ce admixtures. Similar data for InP:Zn are given for comparison.

Similar behaviour of samples grown with the admixture of Ce and Yb is clearly seen. In addition, layers doped with Ce exhibit a very slow decay of conductivity when they are cooled to temperatures below 60 K, the behaviour previously observed on layers grown with Yb admixture [5]. Based on this observation and the fact that Ce has been incorporated into the InP lattice [6], we suggest that the dominant impurity responsible for *p-type* conversion in these layers is Ce itself.

Hole concentrations of InP layers grown with the addition of Tm_2O_3 , Eu_2O_3+Tb and Eu_2O_3+Dy are shown in Fig. 2.

Binding energies of dominant acceptors responsible for *n*→*p* conductivity conversion are determined as 160, 72 and 72 meV for Tm_2O_3 , Eu_2O_3+Tb and Eu_2O_3+Dy additions, respectively. The origin of these impurities or defects remains to be clarified.

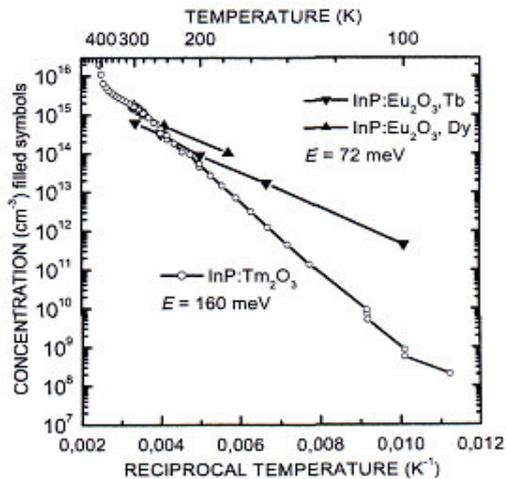


Fig.2 Hole concentration as a function of reciprocal temperature for InP layers grown with Tm_2O_3 , Eu_2O_3+Tb and with Eu_2O_3+Dy admixture.

Low-temperature PL spectra of layers grown with Tm_2O_3 admixture exhibit a broad band at 975 nm (1.27 eV) that corresponds to the above mentioned binding energy 160 meV. Long wavelength parts of PL spectra measured at 3.5 K are shown in Fig. 3 for layers grown with the admixture of Tm_2O_3 —curve (a), the simultaneous admixture of Eu_2O_3+Dy —curve (b) and Eu_2O_3+Dy —curve (c).

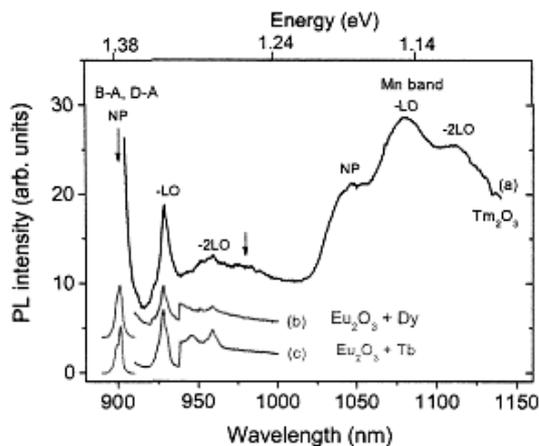


Fig.3 Long wavelength parts of low-temperature PL spectra of InP layers prepared with Tm_2O_3 , $Eu_2O_3 + Tb$ and $Eu_2O_3 + Dy$ by curves (a), (b) and (c), respectively.

Two types of radiative transitions are shown: (1) sharp band (B-A, D-A) at 1.38 eV related to shallow acceptor transitions with its one and two phonon replicas and (2) a broad band due to Mn with no-phonon line at 1.18 eV. Mn band is observed, with varying intensity, in most studied layers. No radiative transitions corresponding to binding energies 72 meV have been found on samples with Eu_2O_3+Tb and Eu_2O_3+Dy admixtures.

However, observation of radiative transitions possibly connected with energy level corresponding to binding energy 72 meV would be obscured by the overlap of such transitions with one phonon replica

(-LO) of the strong band due to shallow acceptor transitions.

4. CONCLUSION

High purity and Ce doped InP layers were grown on InP:Sn and InP:Fe substrates using LPE with Tm, Tm_2O_3 , Eu_2O_3 and Ce admixtures to the growth melt. Temperature dependent Hall measurements yield the binding energy 31 meV for dominant acceptor responsible for *p-type* conductivity of layers prepared with Ce addition, Arrhenius plots of hole concentration versus reciprocal temperature for layers doped with Ce show similar slope as those doped with Yb and layers doped with Ce exhibit a very slow decay of conductivity when cooled below 60K, a phenomenon observed previously on Yb doped layers. Thus we conclude that the dominant impurity responsible for *p-type* conductivity is Ce itself. Dominant acceptors that cause the conductivity change in the case of Tm, Tm_2O_3 and Eu_2O_3 admixture remain to be identified.

PL spectra of layers grown with the admixture of Tm and RE oxides allowed distinguishing the band-acceptor transitions from donor-acceptor pair ones, and enabled identification of exciton related transitions. Co-admixture of Tb and Dy with Eu_2O_3 did not prove to be useful in growing pure samples with effective $n \rightarrow p$ conversion. Actually the resolution of both excitonic and shallow acceptor related transitions deteriorated when co-admixture was used.

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