JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 5, May 2007, p. 1221 - 1226

Invited Paper

InP p-type epitaxial layers grown with the addition of rare-earth elements for use in radiation detection

J. ZAVADIL*, O. PROCHAZKOVA, K. ZDANSKY, P. GLADKOV
Institute of Radio Engineering and Electronics, Academy of Sciences of the Czech Republic, Chaberská 57, 182 51 Praha 8, Czech Republic

InP single crystal layers were grown by liquid phase epitaxy on semi-insulating InP:Fe and *n*-type InP:Sn substrates with Ce, Pr, Tm, Tm_2O_3 and Yb additions to the growth melt. Grown layers were examined by low-temperature photoluminescence spectroscopy, C-V and temperature dependent Hall measurements. An efficient purification due to rare earth (RE) admixture has been observed and all reported layers exhibit the change of electrical conductivity from *n* to *p* at certain RE concentration in the melt. The highest purifying effect has been found for Pr and Tm_2O_3, where the impurity concentration was decreased by up to three orders of magnitude and fine luminescence spectral features were revealed. Ce and Yb were found as dominant acceptor impurities responsible for *n* to *p* type electrical conductivity change, while the dominant acceptor responsible for the conductivity crossover in the case of Tm and Tm_2O_3 admixtures remains to be identified.

(Received November 14, 2006; accepted April 12, 2007)

Keywords: Rare-earth elements, InP epitaxial layers, Hall measurements, Low-temperature photoluminescence

1. Introduction

Materials containing rare-earths (RE) represent a rapidly developing field of research. Inspired by the spectacular results obtained on RE doped silica fibres which function as excellent fibre lasers and optical amplifiers [1] there has been a revival of interest in the behaviour of RE admixtures in silicon [2] and III-V compound semiconductors [3]. This increased interest in RE in the context of semiconductor and glass materials has been motivated by two characteristic properties of RE elements: a sharp luminescence from screened inner shells (4f - 4f transitions) practically independent on the host, and a strong tendency to form oxides as well as compounds with elements of the 5th and the 6th rows of the Periodic Table of the Elements.

The exclusive position of RE in the Periodic Table of the Elements is consequent upon the uppermost electron configuration $5s^2 5p^6 6s^2$ that these 14 elements share. They are hence projected on the same site – that of lanthanum. The inner 4f shell is being filled in the progression from lanthanum ($4f^0$) to lutetium ($4f^{14}$). If an atom or ion of RE element is embedded in a host lattice, the spin-orbital degeneracy of the 4f levels is lifted by the crystal field. Electron transitions between these levels are well shielded from external influences by the outer electron shells. Both, the sharp luminescence transitions and the gettering efficiency make RE promising candidates for investigation and applications in opto- and micro-electronics; for example light emitting devices, and sufficiently pure materials for further use.

RE doped III-V compounds are attractive materials because they have the potential to combine the advantages of optical properties of RE^{3+} ions and the electronic properties of semiconductor hosts. The use of semiconductor hosts enables to utilize minority carrier injection to excite the RE 4f shell in excess of direct [4] or indirect [5] photoexcitation. A successful excitation of the inner RE 4f shell by minority carrier injection has been reported for Er-doped GaAs [6] and Yb-doped InP [7]. There have been high expectations in recent years connected with RE elements, sometimes called f-elements, as promising sources of sharp and temperature independent radiation after their incorporation into the active layer of the light-emitting semiconductor device. Erbium (Er) and Ytterbium (Yb) were the most studied RE elements [6-10] in this context. In most cases, however, the atoms or ions of f-elements just do not enter the substitutional or interstitional sites of the host lattice [11, 12] due to their larger ionic radii and low solubility in the growth melt. Nevertheless, the strong chemical reactivity can lead to useful results - the gettering of undesirable impurities that habitually form shallow donors. The possibility to use these elements as efficient agents to getter off undesirable residual impurities was suggested a long time ago [13]. This effect has been studied in detail for InP epitaxial layers in our laboratory [11, 14, 15] and elsewhere [16] recently.

InP single crystals, both bulk and thick epitaxial layers, are promising materials for the preparation of radiation detectors operating at room temperature. The room temperature operation is possible due to sufficiently wide bandgap energy (E_g=1.34 eV) at room temperature and high mass density (ρ=4.8 gcm^{-3}). The high value of atomic number (Z_{In}=49) for at least one of the constituent atoms predicates a high stopping power which for a high energy photon is proportional to Z^n ($n \approx 4 \div 5$). The absorption capacity of InP for 60 keV photons is about a factor of three higher than that of the much studied and as to the cost nearly equivalent GaAs.

High purity InP with shallow impurity concentration below 10^{15} cm^{-3} is needed in the context of radiation detectors [17] to exploit the above mentioned potential of InP material. Therefore the preparation of thick InP layers of high purity is of great importance for radiation detection, i.e. for allowing electrons and holes, originating from the electron-hole pairs created during the radiation impact, to reach collecting electrodes. As suggested earlier [11] the preparation of Schottky type collecting (and/or blocking) contacts [17] would be of great advantage for performance of detectors. At present Schottky contacts on the *p-type* InP could be prepared with large height and low leakage current which could not be reached on the *n-type* InP. Thus the preparation of pure *p-type* InP epitaxial layers without intentional doping with shallow acceptors is of importance.

In recent years we have pursued the investigation of the influence of the admixture of rare-earths in the growth melt, on electrical and luminescence properties of InP epitaxial layers [11, 14, 15, 18]. Among the studied RE elements and oxides (Ce, Pr, Nd, Sm, Eu, Eu_2O_3, Tb, Dy, Ho, Er, Tm, Tm_2O_3, Yb and Lu) in our laboratory, only Yb and Ce have been incorporated into the InP lattice [15, 18]. It turns out that the admixture of Ce, Pr, Tb, Dy, Yb, Tm, Tm_2O_3 and Eu and Eu_2O_3 leads, at certain concentrations, to the reversal of InP conductivity type from *n* to *p*. Dy was shown [11] to produce the conductivity conversion at lowest concentration thus giving the best opportunity to grow thick, pure and structurally perfect layers. Detailed studies of the temperature-dependent Hall effect and low-temperature photoluminescence (PL) enabled to identify the dominant acceptors responsible for the conductivity crossover in the case of Pr, Tb, Yb and Ce additions. From these studies we determined Ge [14], Mn [15], Yb [15] and Ce as dominant impurities in the case of Pr, Tb, Yb and Ce additions, respectively.

In this paper we review our investigation of the lanthanide series in the context of the LPE growth technology, and we report the effect of $n \rightarrow p$ conductivity conversion for layers grown with the admixture of Yb, Ce, Tm and Tm_2O_3. The temperature dependent Hall effect and low-temperature PL spectroscopy have been used to identify the dominant acceptors responsible for the conductivity crossover, or to determine their characteristic parameters. The purification of InP epitaxial layers due to Pr admixture is demonstrated on low temperature exciton and near band-gap PL spectra.

2. Experimental

The InP layers were prepared by the LPE method, which is particularly suitable for growing relatively thick ($d \geq 10$ μm) layers, as the present context requires. The single crystal layers were grown on (100) oriented InP:Sn and/or semi-insulating InP:Fe substrates. Growth melts consisted of 6N purity In, InP poly-crystals and RE admixtures. RE were added to the melts in the form of a metal or oxide, and their concentrations varied within 0.008 – 1.4 at%. The epitaxial growth was initiated at temperature 645 °C using super-cooling technique with cooling rate 0.8°Cmin^{-1}, even though the super-saturation temperature ΔT of the solution can not be evaluated precisely. The formation of RE pnictides in the liquid phase and their subsequent slugging increases the phosphorus deficit. Since the growth is usually performed from over-saturated solutions, this effect must be taken into consideration.

The dependence of the quality of the interface between epilayer and substrate, the layer thickness, overall surface morphology and density of structural defects on the growth conditions and RE additions were monitored employing optical microscopy and scanning electron microscopy (SEM). Rough estimates of the electrical properties on the contact-less samples were gained from C-V measurements performed with the mercury probe. More substantial were results of temperature-dependent Hall effect measurements on contacted samples in the van der Pauw configuration. The set enables to work in the temperature range 6.5-320 K. Comparing data collected at room temperature with those measured at 77 K as well as with theoretical values, active donor N_d and acceptor N_a concentrations were evaluated. Photoluminescence spectra were taken at various temperatures and various levels of excitation by He-Ne, Ar-ion and 657 nm LD lasers in the optical closed-cycle He cryostat enabling measurements in the temperature range 3.5-300 K. The 1 m focal length monochromator coupled with thermoelectrically cooled GaAs photomultiplier and liquid nitrogen cooled high-purity Ge detection system enables sensitive and high resolution measurements in the spectral range 400 – 1700 nm by using lock-in technique. A specially designed set-up consisting of Oriel monochromator 77250 and liquid nitrogen cooled InSb detection system and coupled with all mirror optics to the optical He cryostat was used for measurements in mid-infra-red spectral range 2000 – 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 element 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 element 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 elements. The admixture of Tm_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. Layers prepared with the admixture of Ce were found to be of *p*-type conductivity while layers grown with Pr, Tm, Tm_2O_3 and Yb addition exhibited *n→p* type conductivity conversion at certain concentration of RE in the melt.

Temperature and excitation power dependence of PL spectra have been investigated in the near band-gap region to monitor the influence of RE addition to the growth melt. The major manifestation of RE admixture is considerable narrowing of the spectral bands and the corresponding appearance of fine spectral features, characteristic of pure material, low in defects. This effect has been found to be most pronounced for Pr, Tm and Tm_2O_3. The observed radiative transitions in InP samples for all studied RE elements could be grouped into three cathegories: band-edge (BE) transitions at about 1.418 eV (874nm), shallow impurity related transitions at 1.38 eV (898 nm) and deep-level transitions at 1.14 eV (1087 nm) [19]. Typical low-energy PL spectra of InP grown with the addition of Pr, and covering excitonic band and shallow acceptor related transitions are shown in Fig. 1 for four levels of excitation power. The high energy band (BE) in Fig. 1 exhibits superlinear behaviour with increasing excitation power and results from the decay of excitons. The peak at 1.38 eV which is usually an unresolved convolution of band-acceptor (B-A) and donor-acceptor pair (D-A) transitions deserves more attention. A temperature dependence of the shallow-acceptor related bands has been studied for the low excitation power densities, when the double peak nature of the band is distinctly resolved. From the inspection of these curves we would assign the low-energy peak to D-A transitions since it decays quickly with increasing temperature as compared to the high-energy peak assigned to band-acceptor transitions (B-A). This is in accord with the observation that the D-A subpeak shifts to the higher energy with increasing excitation power density.

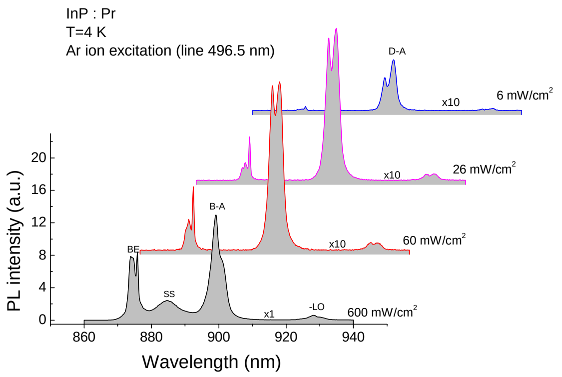

Fig. 1. Low-temperature PL spectra taken at four levels of excitation power, ranging from 6 to 600 meV. Fine structure of excitonic band at 875 nm (1.418 eV) is clearly seen and also shallow acceptor related transitions originating from band to acceptor (B-A) and donor-acceptor pair (D-A) transitions are clearly resolved at 900 nm (1.38 eV). The saturation of D-A subpeak with an increasing level of excitation is demonstrated.

Low temperature spectra taken at various levels of excitation power (Fig. 1) reveal that D-A subpeak saturates more quickly with increasing level of excitation in comparison with the B-A subpeak. This behaviour could be understood using the schematic diagrams [20] of electron transitions involved in D-A and B-A recombinations. Both the transitions of electrons from the conduction band to donor levels and from acceptor levels to the valence band are rather quick as compared to the radiative D-A recombination. However, since the D-A recombination is relatively slow process, transitions from the conduction band to donor levels are saturated with increasing level of excitation and consequently the D-A process saturates more quickly as compared to B-A transitions. As mentioned earlier we report the simultaneous observation of the conduction band to acceptor (B-A) and donor-acceptor (D-A) pair transitions. This allows the optical determination of individual binding energies for donor and acceptor states involved, by using the following formulas [20]:

$$E_D = (h\nu)_{B-A} - (h\nu)_{D-A} + \frac{e^2}{\varepsilon r} - \frac{1}{2}kT \qquad (1)$$

$$E_A = E_g - (h\nu)_{B-A} + \frac{1}{2}kT$$

The quantities $(h\nu)_{B-A}$ and $(h\nu)_{D-A}$ represent the measured energies of *B-A* and *D-A* transitions, respectively. E_g is the band gap energy and T is the electron temperature estimated as 25 K for lattice temperature 4 K [21]. The Coulomb term $e^2/\varepsilon r$ can be obtained for the limits of strong and weak excitation as 5.95 meV and 2.8 meV, respectively. With these Coulomb energies and equation (1) donor and acceptor binding energies are found as $6.8\ \text{meV} < E_D < 7.8\ \text{meV}$ and $E_A = 47$ meV. These binding energies are in good agreement with published data indicating that the shallow acceptor responsible for observed optical transitions is carbon.

Fine structure of the excitonic band is shown in more detail in Fig. 2 where band gap energy together with transitions corresponding to free and impurity bound excitons are indicated. Well resolved excitonic band is an evidence of good quality of prepared layers. Free exciton binding energy has been found to be 5.3 meV.

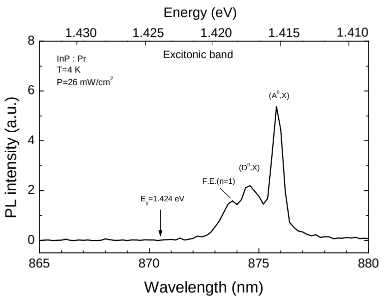

Fig. 2. Low-temperature PL spectrum of InP:Pr layer. Excitonic band at low excitation level is shown. Low temperature band gap energy E_g is indicated by an arrow. Narrow bands corresponding to the decay of free exciton (FE), exciton bound to neutral donor (D^0X) and exciton bound to neutral aceptor (A^0X) are well resolved.

The conversion of electrical conductivity from *n→p* due to RE admixture to the growth melt will be discussed for Yb, Ce, Tm and Tm_2O_3. Temperature dependent Hall measurements of *p-type* InP layers grown with Ce and Yb admixtures have been performed in the range from room temperature to about 35 K. Below this threshold temperature the conductivity of samples changes very slowly so that 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, measured by thermometers in the cryostat, is stabilised within 0.05 K the decays of conductivity lasting from minutes at 60 K to an hour at 35 K are monitored. The InP(Ce, Yb) samples approach a metastable state at temperatures below 35 K and results of Hall measurements are not reliable any more.

Hole concentration and mobility for InP layers grown with the admixture of Ce and Yb are shown in Fig. 3 together with corresponding data on InP:Zn, for comparison.

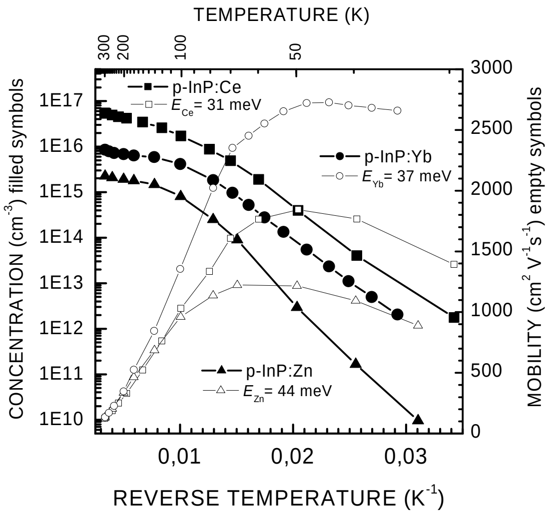

Fig. 3. Hole concentration and mobility for InP layers grown with Yb and with Ce admixtures together with data for InP:Zn.

The curves of hole concentration reveal straight lines at low temperatures giving the binding energy (after the $T^{3/2}$ correction) of the dominant acceptors equal to 31 meV and 37 meV for Ce and Yb, respectively.

We have observed the sharp 4f-4f radiative transitions resulting from inner shells of Yb^{3+} and Ce^{3+} ions in PL spectra of InP layers grown with the addition of these RE elements. This observation gives a direct proof of Yb and Ce incorporation into the InP lattice. The sharp luminescence bands due to crystal field split inner shell $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transitions of Yb^{3+} ion measured at 4 K are shown in Fig. 4. The crystal field splitting is small compared to the spin-orbit splitting due to the screening of the 4f states by outer closed $5s^2$ and $5p^6$ shells. The labelling of lines in Fig. 4 is according to that used in [22].

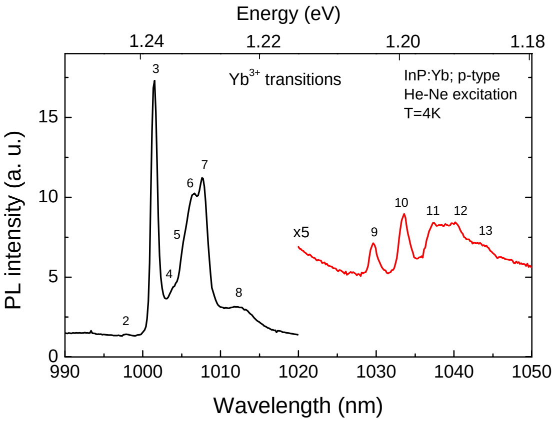

Fig. 4. Low-temperature PL spectrum of Yb^{3+} ion from a typical InP:Yb layer. The sharp luminescence lines arising from crystal field split of $^2F_{5/2}\rightarrow{}^2F_{7/2}$ inner shell transitions are shown.

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 characterised by one 4f electron, the Yb^{3+}ion has thirteen 4f electrons, thus the two elements have a somewhat complementary position within lanthanide series. The low-temperature PL spectrum of InP:Ce layer measured in the mid-infra-red range is shown in Fig. 5. The sharp peak at 0.3507 eV (3534 nm) due to $^2F_{7/2}\rightarrow{}^2F_{5/2}$ transition of Ce^{3+} ion is shown together with the fine structure due to crystal field splitting. The sharp sub-peaks labelled 1 to 5 are due to crystal field splitting and are reported for the first time. The origin of broader sub-peaks 6 and 7 is to be clarified.

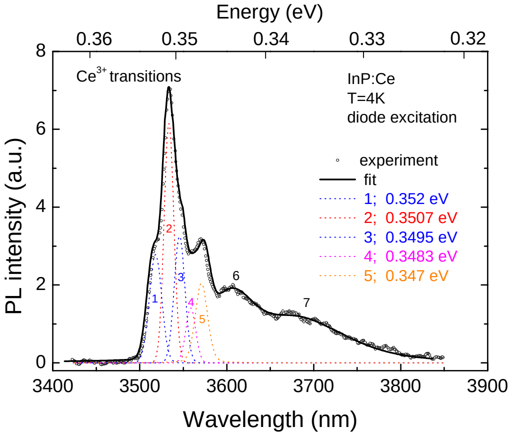

Fig. 5. Low-temperature PL spectrum of Ce^{3+} ions incorporated into the InP layer. A sharp inner shell $^2F_{7/2}\rightarrow{}^2F_{5/2}$ transition of Ce^{3+} ion at 0.3507 eV is clearly seen together with crystal field splitting.

The Yb impurity in InP is known [23] to be incorporated as a cubic Yb^{3+} centre on the cation site (In).

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 large difference between electro-negativities of Yb, Ce and In. We suggest that a potential barrier raised by this interaction is responsible for the observed metastability of electrical conductivity. In view of similar electrical behaviour of InP layers doped with Ce and Yb, particularly the metastable behaviour of electrical conductivity below 35 K and of the incorporation of Ce^{3+} and Yb^{3+} ions into InP host, we conclude that the Ce and Yb [15] themselves are the dominant acceptors responsible for *n→p* conductivity conversion of InP:Ce, Yb layers.

Hole concentration and mobility for InP layer grown with the addition of Tm_2O_3 are given in Fig. 6 together with corresponding data measured on InP:Mn sample, for comparison. A binding energy of dominant acceptor responsible for *n→p* conductivity conversion is determined as 160 meV, in the case of Tm and Tm_2O_3 admixture.

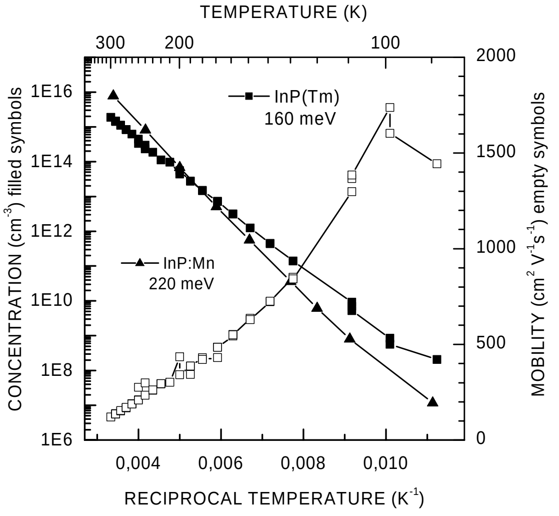

Fig. 6. Hole concentration and mobility for InP layers grown with Tm admixture together with those for InP:Mn, for comparison.

Low-temperature PL spectra of these samples exhibit a broad band at 960 nm (1.29 eV) that fairly well corresponds with measured binding energy of about 160 meV. The long-wavelength parts of PL spectra, for layers prepared with the additions of Tm_2O_3 and Eu_2O_3, measured at 3.5 K, are shown in Fig. 7 by curves (a) and (b), respectively. The spectrum of Eu_2O_3 is shown for comparison. In addition to characteristic broad band due to Mn at 1070 nm (1.14 eV) observed for both RE oxides, another broad band at 960 nm is observed on samples grown with Tm_2O_3 admixture.

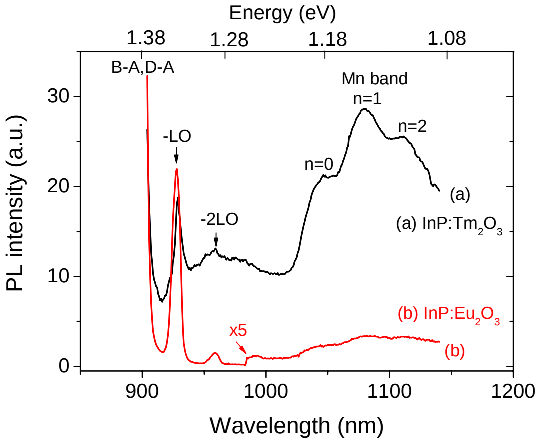

Fig. 7. Long wavelength parts of low temperature PL spectra of InP layers prepared with Tm_2O_3 and Eu_2O_3 admixtures are shown, by curves (a) and (b), respectively. An additional broad band at 960 nm is clearly seen on layers prepared with Tm_2O_3 admixture. The band overlaps with the two phonon replica of shallow acceptor band B-A, D-A labeled as (-2LO).

4. Conclusions

High purity and Ce and Yb doped InP layers were grown on InP:Sn and InP:Fe substrates using LPE with Ce, Pr, Tm, Tm_2O_3 and Yb admixtures, and have been characterised by electrical and optical methods. All reported types of epitaxial layers exhibit *n→p* conductivity crossover at certain level of RE admixture. Studies by photoluminescence and Hall effect show that RE presence in the growth process leads to pronounced gettering of shallow impurities. As a consequence, free-carrier and shallow impurity concentrations are reduced by up to three orders of magnitude, the PL spectra are markedly narrowed and fine spectral features are resolved. We would like to point out that in the case of Pr and Tm_2O_3 admixture in the growth melt the donor - acceptor pair (D-A) transitions could be clearly resolved from band-to-acceptor (B-A) transitions.

Temperature dependent Hall measurements yield the binding energies 31 meV and 37 meV for dominant acceptors responsible for *p-type* conductivity of layers doped with cerium (Ce), and ytterbium (Yb), respectively. Arrhenius plots of hole concentration versus reciprocal temperature for both these layers show similar slope and both exhibit a very slow decay of conductivity when cooled below 60 K, a phenomenon observed previously on Yb doped layers [15]. Thus we conclude that the dominant impurities responsible for *p-type* conductivity are Ce and Yb themselves. The dominant acceptor impurity or defect responsible for conductivity conversion in the case of Tm and Tm_2O_3 has binding energy 160 meV that corresponds fairly well with a broad luminescence band observed at 960 nm. The origin of this impurity or defect remains to be clarified.

Acknowledgement

The work was supported by the Grant Agency of CR, project No.102/06/0153 and by the project No. AV0Z20670512.

References

[1] B. J. Ainslie, J. Lightwave Technol. **9,** 220 (1991).
[2] A. Polman, G. N. van den Hoven, J. S. Custer, J. H. Shin, R. Serna, P. F. A. Alkemade, J. Appl. Phys. **77,** 1256 (1995).
[3] J. M. Zavada, D. Zhang, Solid State Electronics **38,** 1285 (1995).
[4] Rare Earth Doped Fiber Lasers and Amplifiers, ed. M. J. F. Digonnet, Marcel Dekker, Inc., New York 1993 (Optical Engineering vol. 37).
[5] A. Taguchi, K.Takahei, Y. Horikoshi, J. Appl. Phys. **76**, 7288 (1994).
[6] P. S. Whitney, K. Uwai, H. Nakagome, K. Takahei, Electron. Lett. **24**, 740 (1988).
[7] W. H. Haydl, H. D. Müller, H. Ennen, W. Körber, K. W. Benz, Appl. Phys. Letters **46**, 870 (1985).
[8] M. C. Wu, C. M. Chiu, Y. K. Tu, J. Electrochem. Soc. **140**, 3030 (1993).
[9] K. Takahei, A. Taguchi, J. Appl. Phys. **78**, 5614 (1995).
[10] Y. Fujiwara, A. Koizumi, A. Urakami, T. Yoshikane, K. Inone, Y. Takeda, Mater. Sci. & Engg., **B105**, 57 (2003).
[11] O. Prochazkova, J. Zavadil, K. Zdansky, Cryst. Res. Technol., **36**, 979 (2001).
[12] J. Raczynska, K. Fronc, J. Langer, A. Lemanska, A. Stapor, Appl. Phys. Letters **53**, 761 (1988).
[13] V. F. Masterov, L. F. Zakharenkov, Sov. Phys. Semicond., **24**, 383 (1988).
[14] K. Zdansky, J. Zavadil, O. Prochazkova, P. Gladkov, Mater. Sci. & Engg., **B80**, 10 (2001).
[15] K. Zdansky, O. Prochazkova, J. Zavadil, J. Novotny, Mater. Sci. & Engg., **B91/92**, 38 (2002).
[16] H. H. Gao, Y. V. Sherstnev, Semicond. Sci. and Technol., **4**, 441 (1999).
[17] F. Dubecky, P. Bohacek, B. Zatko, M. Sekacova, J. Huran, V. Smatko, R. Fornari, E. Gombia, R. Mosca, P. G. Pelfer, Nucl. Instr. Meth. A **531,** 181 (2004).
[18] J. Zavadil, O. Procházková, P. Gladkov, Cryst. Res. Technol., **40**, 498 (2005).
[19] T. S. Kim, B. G. Streetman, in: Properties of Indium Phosphide, *INSPEC* EMIS Data reviews Series No. 6, London and New York, (1991), Chapter 9, p. 165.
[20] V. Swaminathan, A. T. Macrader, Materials Aspects of GaAs and InP Based Structures, Prentice-Hall Englewood Cliffs (NJ) (1991), p.282.
[21] J. U. Fischbach, G. Benz, N. Stath, M. H. Pilkuhn, Solid State Comm. **11**, 725 (1972).
[22] W. Korber, A. Hangleiter, Appl. Phys. Lett. **52**, 114 (1988).
[23] M. C. Wu, C. M. Chiu, Y. K. Tu, J. Electrochem. Soc. **140**, 3030 (1993).

---

*Corresponding author: zavadil@ure.cas.cz