INFLUENCE OF RARE-EARTH ELEMENTS ON THE ELECTRICAL AND OPTICAL PROPERTIES OF INP BULK CRYSTALS

Roman YATSKIV, Jiří ZAVADIL, Ladislav PEKAREK

Authors: ***Roman Yatskiv, PhD., Jiří Zavadil, PhD., Ladislav Pekarek, MSc. Eng.***
Workplace: ***Institute of Photonics and Electronics, Academy of Sciences of the Czech Republic***
Adress: ***Haberská 57, 182 51, Praha 8, Czech Republic***
Phone: ***+420 266773423***
E-mail.:

Abstract

We report on the influence of rare earth (RE) elements (Pr, Er, and Dy) addition during vertical Bridgman low pressure synthesis on the properties of InP crystals. The temperature dependent Hall measurement and low temperature photoluminescence (PL) spectroscopy were employed to study the changes in electrical and optical properties of the crystals. Quantitative analysis of dominant impurities was studied using secondary ion mass spectrometry (SIMS). The observed changes are attributed to the gettering effect of REs caused by the high affinity of REs towards shallow impurities in InP.

Key words

InP, Crystal growth, REEs elements, Electrical properties, Photoluminescence, SIMS

Introduction

The semi-insulating (SI) InP has important applications in the fields of optoelectronics, integrated optics, and high frequency devices. It is also promising material for the room temperature X, γ and particle detectors [1-4]. Commercial SI InP wafers have been obtained reproducibly only with Fe doping during the crystal growth process. The mid-gap position of the $Fe^{3+/2+}$ acceptor, located 0.65 eV below the conduction band [5, 6] makes it possible to obtain SI InP with resistivity above 10^7 Ωcm. However, doping inhomogeneities due to iron segregation, iron diffusion from the substrate to epilayers, large electron and hole capture rates, and creation of FeP_2 precipitates at highest Fe concentration in the crystal are known to have negative impact on the device performance. To achieve lower Fe concentration, a co-doping with Fe and Zn [7] was used. Fe-doped InP material can also be improved by co-doping with Ga, which is reducing the dislocation density, as proposed by Clerjaud [8]. Thermal stability of Fe and Ga doping of InP was shown in [9, 10]. It has been shown that the addition of Ga impurities is effective for growing semi-insulating Fe-doped InP crystals having a low dislocation density but due to high segregation coefficient of Ga in InP the free-dislocation part is only localized in the upper zone of InP: (Ga,Fe) crystals. Transition metal (TM) acceptors, such as Cr [11] and Co [12, 13] have been also used to compensate the residual shallow donors in InP, but their respective levels are located 0.4 eV below the conduction band [14] and 0.3 eV above the valence band [15], and this makes it impossible to achieve resistivity higher than 10^5 Ωcm. SI InP obtained with Ti doping was presented in [16]. Ti acts as a deep donor located 0.63 eV below the conduction band. Ti doped SI InP should exhibit far greater thermal stability than Fe-doped InP due to smaller capture rate and lower diffusivity. Another possibility is co-doping with TM donors and shallow acceptors. This idea was proposed in [8]. SI crystal of Cr-doped InP co-doped with Cd and Hg with resistivities up to 10^6 Ωcm, were growth and reported in [17], however the thermal stability of Cr in InP is similar to that of Fe. SI crystals of Ti-doped InP co-doped with Hg [17, 18], Be, Cd, Zn [19, 20], and Mn [21] with resistivities about 10^6 Ωcm and very high thermal stability were presented.

Alternative approaches to the preparation of SI InP are high temperature annealing of undoped InP in pure phosphorus or iron phosphide ambient [22, 23]. To further improve the quality of SI substrates, availability of high purity input material is an essential prerequisite. Diminished concentrations of unintentional impurities in bulk crystals allow to use lower concentrations of TM necessary to reach the SI state. Using rare earth (RE) elements can be one of the promising ways for further improvement of substrate materials. Strong motivation to study REs in the InP is connected with their high chemical reactivity and reduction capability. A number of elements (for example Si, O, S and C), which act as dopants in InP form stable compounds with REs. Since these compounds are insoluble in In, REs can be used to remove these impurities from the growth melts and reduce the background electron concentration of the grown crystals. Intensive investigation of the application of REs in III-V compounds, both for bulk crystals and epitaxial films, started in the 1980s. First application of REs was the exploitation of their specific luminescence properties when incorporated into the lattice of the crystalline semiconductor material. RE doped semiconductors show sharp luminescence due to the intra-4fshell transitions resulting in luminescence in the region of 1.0 and 1.54 μm suitable for optical communications. Luminescence studies of InP:Yb LPE layers, first reported by Zacharenkov et. al. [24], have shown that the REs behaved as the isovalent impurities within crystal lattice. These results were later confirmed by W. Korber et al. [25]. InP:Yb crystal growth by the method of synthesis-solute diffusion were investigated by Stapor et al, [26] Extended studies of the influence of REs on electro-optical parameters of InP bulk crystals have also been reported [27, 28]. The question whether REs create new charged centers in the semiconductor materials or only change their electrical properties due to the formation of neutral complexes with residual impurities has not been answered so far.

In this paper, we report on the growth of Pr, Dy, and Er treated InP crystals by a modified vertical Bridgman method, and on the investigation of their electrical and optical properties.

Technology of the crystal growth

The initial polycrystalline InP was synthesized and grown from 6N purity In and P by a modified vertical Bridgman method using conical quartz crucibles placed inside a sealed evacuated quartz ampoule. Schematic picture of the experimental set up shows Fig.1. The growth temperature was kept at 980 °C and the temperature gradient was 25 °C/cm. The phosphorus temperature was 450 °C, corresponding to the phosphorus vapor pressure of about 0.1 MPa. The crystals were grown conventionally as well as with Pr, Er, and Dy admixture to the growth melt.

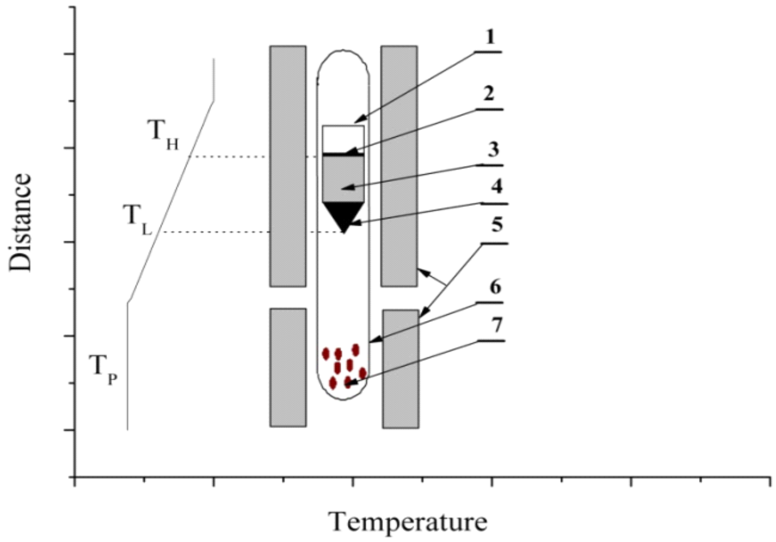

Fig. 1 *Schematic representation of the synthesis method (SSD). 1-melting-pot, 2-interface In-P, 3-liquid solution of In-P-REs, 4- seed InP, 5-resistance furnace, 6-ampoule, 7-solid phosphorus,* T_H*-temperature at the melt surface,* T_L*-temperature at the crystallization front,* T_P*-temperature at the cold end ampoule*

1 mm thick wafers of 8 mm in diameter were cut from the bottom and from the top of the conical crystal ingot and characterized by the measurements of electrical resistivity and Hall coefficient in van der Pauw configuration in the temperature range from the room temperature (RT) to 10 K. PL spectra were taken at various temperatures and various levels of excitation by He-Ne laser in an optical closed cycle He cryostat, enabling measurements in the range 3.5-300 K. The 1 m focal length monochromator with the cooled high purity Ge detector and/or cooled GaAs photomultiplier enables sensitive and high resolution measurement in the spectral range 400-1800 nm using the lock-in technique and the computer controlled data collection.

Experimental result and discussion

Electrical characteristics of bulk InP crystals are shown in Table 1. In the case of conventionally prepared crystals, the electron concentration and mobility at room temperature were $2.9\times10^{15}\,\mathrm{cm^{-3}}$ and $4524\,\mathrm{cm^2V^{-1}s^{-1}}$, respectively. Pr or Er admixture reduced the concentration of residual donors in the samples (Table 1). It may be explained by a strong interaction of REs with the background impurities in the melt. REs act as getters and purify crystals during growth. The best results were observed in the case of Pr and Er admixtures. At the temperature of liquid nitrogen the electron mobility was up to five times higher compared to the conventionally prepared material. It indicates effective binding of shallow donors to RE elements forming neutral complexes. In the case of Dy admixture, no purification effect was observed. Samples prepared with the admixture of Dy are characterized by smaller electron mobility and higher concentration of free electrons compared to the undoped ones. It indicates that the purifying effect does not simply reflect the ionic radius of lanthanide elements. The influence of Pr concentration in the growth melt has been investigated in more detail by temperature dependent Hall measurements. Inceasing Pr concentration from 0.006 wt% to 0.057 wt% results in steadily increasing electron mobility- this behaviour is documented in Table 1.

ELECTRICAL PROPERTIES OF InP CRYSTALS

Table 1

Sample	**RE**	**RE Content (wt.%)**	**Electron concentration n, (cm^{-3})**		**Electron mobility ì, (cm^{2}V^{-1}s^{-1})**	
			300K	**77K**	**300K**	**77K**
InP	-	0	2.9E15	2.7E15	4524	2587
InP	Pr	0.006	1.8E15	1.7E15	4334	1595
		0,028	2.8E15	2.5E15	4149	3375
		0,036	1.9E15	1.8E15	3982	10340
		0,057	1.9E15	2.1E15	3875	27770
InP	Er	0,133	1.8E15	1.7E15	3767	13120
InP	Dy	0,089	4.6E15	4.4E15	3326	4332

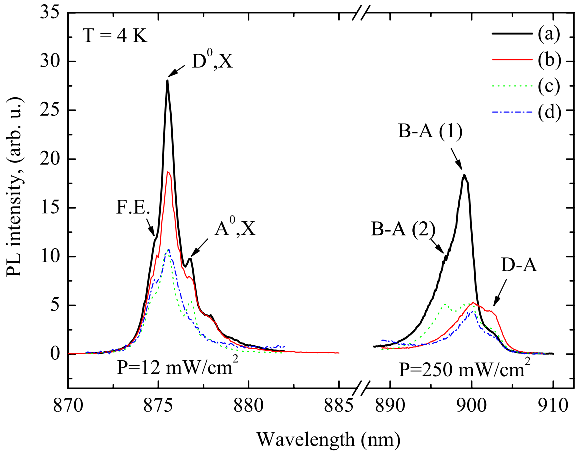

***Fig. 2** Low temperature PL spectra of InP samples prepared with and without RE elements. (a) –InP, (b) – InP:(Dy), (c) – InP:(Er), (d) – InP:(Pr). (F.E.) - free exciton, (D^0,X) - excitons bound to the neutral donor, (A^0,X) - excitons bound to the neutral acceptor, (B-A) – band-acceptor, (D-A) donor-acceptor*

Low-temperature PL spectra of the samples prepared with (the curves (b), (c), (d)) and without REs (curve (a)) are presented in Figure 2. Transitions due to free exciton (F.E.) at 874.6 nm (1.418 eV) and excitons bound to the neutral donor (D^0,X) at 875.5 nm (1.416 eV) or the neutral acceptor (A^0,X) at 876.8 nm (1.414 eV) are well resolved for all samples. The excitonic peak is very sharp for all samples (FWHM < 1 meV), which corresponds well with the high purity of the prepared crystals (n =1.8-4.6x10^{15} cm^{-3}). Transitions described as B-A and D-A are related with shallow acceptors and correspond to conduction band-acceptor and donor-acceptor pair transitions, respectively. The spectra distinguish three subbands for conventionally prepared and REs treated InP samples. The two B-A subbands are tentatively asigned to Zn and C.

The shallow acceptor related spectra taken at various levels of the excitation power are presented in Fig.3. The observed incease of electron concentration in samples grown with the addition of Dy is confirmed by low-temperature PL. It follows from Figs. 2 and 3 that the relative intensity of transitions due to donor-acceptor pairs recombination (D-A sub-band) is by far the strongest in case of Dy admixture – sample (b).

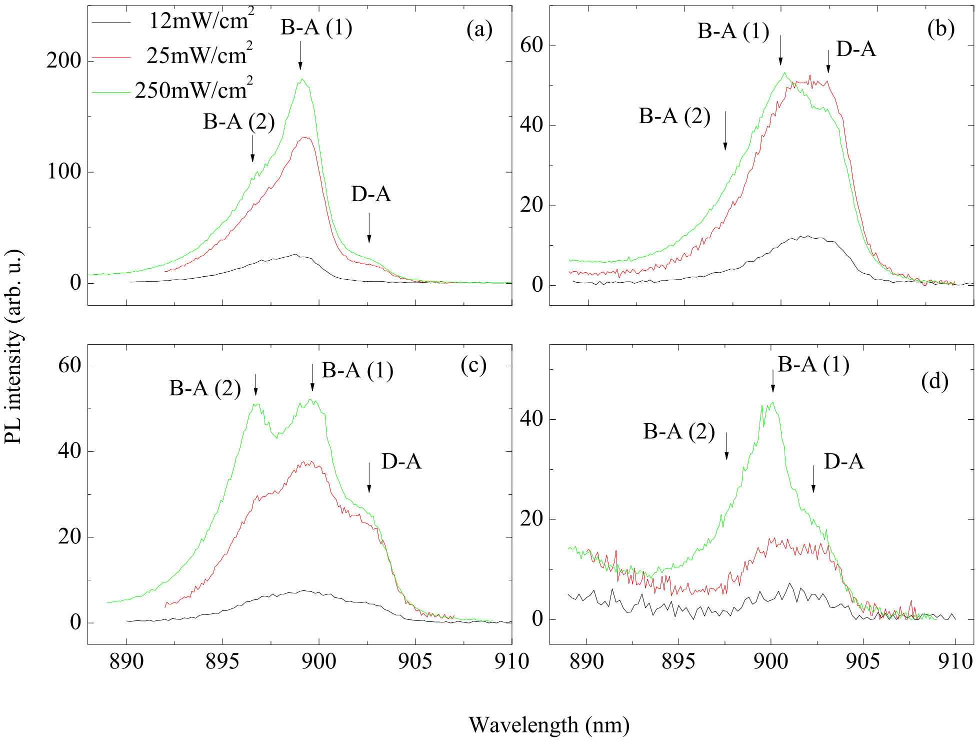

Fig. 3 *Low temperature PL spectra of InP samples prepared with and without RE elements at different level of excitation power. (a) – InP, (b) – InP:(Dy), (c) – InP:(Er), (d) – InP:(Pr). (B-A) – band-acceptor, (D-A) donor-acceptor*

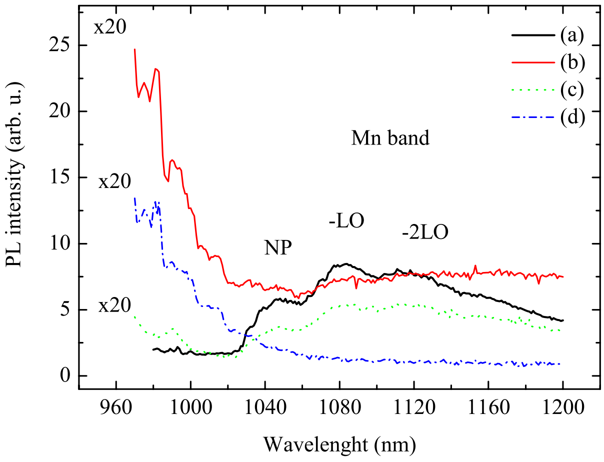

Fig. 4 *Low temperature PL spectra of InP samples prepared with and without RE elements. (a) – InP, (b) – InP:(Dy), (c) – InP:(Er), (d) – InP:(Pr). (B-A) – band-acceptor, (D-A) donor-acceptor*

The long-wavelength part of PL spectra is usually dominated by Mn related band consisting of three partly resolved peaks at 1.191 eV (n 1.149 eV (n=1) and 1.109eV (n=2), which are interpreted as zero phonon line), and one (-LO), and two (-2LO) phonon replicas (Fig. 4). A strong band due to Mn was observed only in the case undoped InP samples (curve (a)). In the case of REEs doped crystals we observed reduced intensity of Mn band (curve (c)) or its complete disappearance (curves (b), and (d).

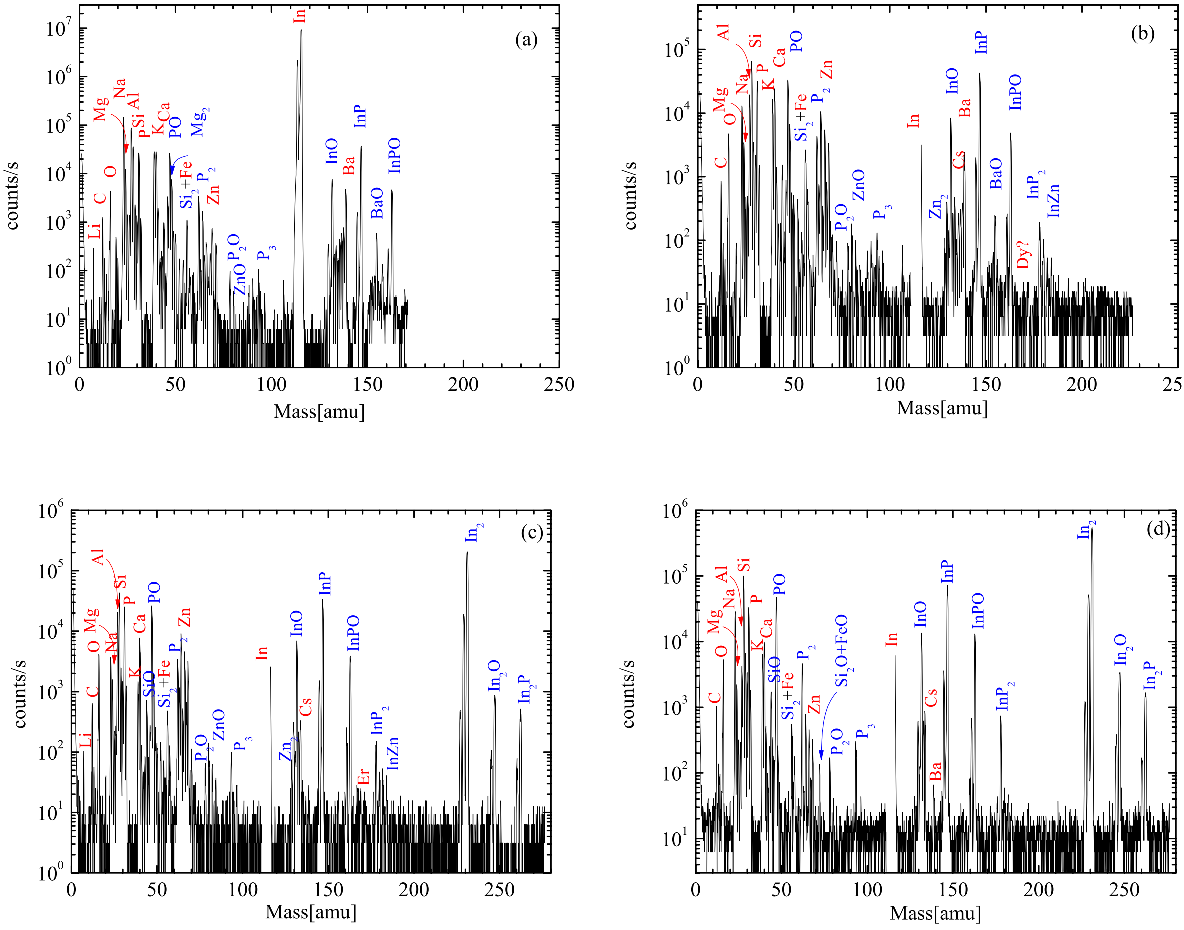

Fig. 5 *Positive secondary ion mass spectrum of samples prepared with and without RE elements. (a) – InP, (b) – InP:(Dy), (c) – InP:(Er), (d) – InP:(Pr)*

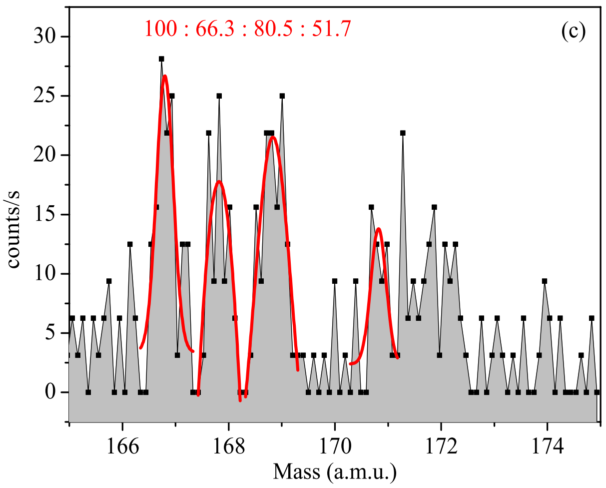

Fig. 6 *Positive secondary ion mass spectrum of Er isotopes. (masses 167, 168, 169 and 171). The experimental Er isotope ratio is shown in the inset.*

Positive secondary ion mass spectrum of InP samples prepared with and without RE elements bombarded with O_2 is presented in Figure 5. In the case of samples (b) and (d) the peaks corresponding to isotopes of Dy and Pr wern't detected. Only in the case of samples (c) were observed peaks corresponding to Er isotopes 167, 168, 169 and 171. The Er isotopes mass spectrum is shown in Figure 6. The experimental isotope ratio (100 : 66.3 : 80.5 : 51.7) and the native one (100 : 68.2 : 79.7 : 44.4), exhibit a good agreement. Due to low Er signal we can assume that the concentration of Er in the investigated samples is of the order of 10^{13} at/cm^3.

Series of polycrystalline InP samples have been prepared by a modified vertical Bridgman method with RE admixtures. Low temperature PL, Hall effect and SIMS measurements indicate that (i) Er, Dy, and Pr are not incorporated into the crystal lattice in the form of electrically and/or optically active centers, (ii) its presence in the growth process leads to pronounced gettering of shallow donor impurities, (iii) the increased electron mobility of InP prepared with Er and Pr admixture is caused by the formation of neutral complexes due to the effective binding of shallow donors and REs.

The admixtures of Pr and of Er have been shown to be the most promising to obtain high purity bulk materials. The use of RE elements can be one of the promising ways for further improvement of InP substrate materials.

Acknowledge

The work has been financially supported by the Academy of Sciences of the Czech Republic with grant KJB200670901. The authors would like to thank J. Lorincik from Institute of Photonics and Electronics, Academy of Sciences of the Czech Republic for SIMS measurements.

References:

[1] J. C. Lund, F. Olschner, F. Sinclair and M. R. Squillante, Nucl. Instr. and Meth. A272 (1988) 885.

[2] F. Dubecky, R. Fornari, J. Darmo, M. Pikna, E. Combia, M. Krempasky, P. G. Pelfer, M. Sekacova, P. Hudek, M. Rucek, Nucl. Instr. and Meth. A408 (1997) 491.

[3] P. Jayavel, S. Ghosh, A. Jhingan, D. K. Avasthi, K. Asokan, J. Kumar, Nucl. Instr. and Meth. A454 (2000) 252.

[4] R.Yatskiv, K.Zdansky, L.Pekarek, Nucl. Instr. and Meth. A598 (2009) 759.

[5] O. Mizuno, H. Watanabe, Electronics Letters, Vol. 11, Issue 5 (1975) 118

[6] G. Iseler, Inst. Phys. Conf. Ser., Vol. 45, Chap. 2 (1979) 144-153

[7] L. Pekarek, K. Zdansky, J. of Cryst. Growth, Vol. 275, Issues 1-2, (2005) e409

[8] B. Clerjaud, J. Phys. C: Solid State Phys. 18 (1985) 3615

[9] R. Coquille, Y. Toudic, L. Haji, M. Gauneau, G. Moisan and D. Lecrosnier, J. of Cryst. Growth, Vol. 83, (1987) 167

[10] L. Haji, R. Coquille, M. Gauneau, Y. Toudic, J. of Cryst. Growth, Vol. 82, Issue 3, (1987) 487

[11] B.W. Straughan, D.T.J. Hurle, K. Lloyd, J.B. Mullin, J. of Cryst. Growth, Vol. 21, Issue 1, (1974) 117

[12] B. Cockayne, W. R. MacEwan, G. T. Brown, J. of Cryst. Growth, Vol. 55, Issue 2, (1981), 263

[13] K. L. Hess, S. W. Zehr, W. H. Cheng, J. Pooladdej, K. D. Buehring and, D. L. Wolf, J. of Cryst. Growth, Vol. 93, Issues 1-4, (1988) 576

[14] G. Bremond, G. Guillot, A. Nouailhat, et. al., J. of Appl. Phys. Vol. 59, Issue 6, (1986) 2038

[15] M.S. Skolnik, R.G. Humphreys, P.R. Tapster, et. al., Journal of physics C-Solid State Physics, Vol. 16, Issue 36, (1983) 7003

[16] C. D. Brandt, A. M. Hennel, L. M. Pawlowicz, et. al, Appl. Phys. Lett. Vol.48, Isuue 17, (1986), p. 1162-1164

[17] Y. Toudic, R. Coquille, M. Gauneau, G. Grandpierre, L. Le Marechal, B. Lambert, J. of Cryst. Growth, Vol. 83, Issue 2, (1987), 184

[18] B. Lambert, Y Toudic, G. Grandpierre, M. Gauneau and B. Deveaud, Semicon. Sci. Technol., Vol. 2, No. 2, (1987), 78

[19] G. W. Iseler, Brian S. Ahern, Appl. Phys. Lett., Vol. 48, (1986) 1659

[20] A. Katsui, Journal of Crystal Growth, Vol. 89, Issue 4, (1988), 612

[21] K. Zdansky, L. Pekarek, V. Gorodynskyy, and H. Kozak, Cryst. Res. Technol. , Vol. 40, (2005) 400\

[22] D. Hofman, G. Müller and N. Streckfuss, Appl. Phys. A, vol. 48 (1989) 315

[23] R. Fornari, A. Brinciotti, E. Gombia, R. Mosca, A. Sentiri, Material Sci. and Engin., vol.B28, (1994) 95

[24] L. F. Zakharenkov, V. A. Kasatkin, F. P. Kesamanly, B. E. Samorukov, M. A. Sokolova, Sov. Phys. Semicond. 15 (1981) 1631

[25] W. Korber, J. Weber, A. Hangleiter, K. W. Benz, H. Ennen and H. D Muller, J. Cryst. Growth 79 (1986) 741

[26] A. Stapor, J. Raczynska, Przybylinska, A. Sienkiewicz, K. Fronc and J. M. Langer, Mat. Sci. For. 10-12 (1986) 633

[27] L. F. Zakharenkov, V. F. Masterov, O. D. Khokrayakova, Sov. Phys. Semicond. 21 (1987) 347

[28] R. Yatskiv, J. Grym, K. Zdansky, L.Pekarek, J. Zavadil, in:International Conference on IPRM, (2009) 91