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Photoluminescence Study of Growth-Related and Processing-Induced Defects in Indium Phosphide

By

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Low-temperature photoluminescence (PL) spectra of 100 keV He^+-implanted n-InP single crystals as well as of 5 MeV α-irradiated n-InP crystals and epilayers have been studied. The radiation-treatment-induced decrease in intensity of bound-excitonic emission was found to be more pronounced than that of free-exciton recombination and luminescence related to deep levels. A new band at 1.399 eV was observed in α-irradiated InP epilayers and attributed to defect complexes involving In_P antisite. The influence of post-implantation annealing in the temperature interval 400 to 750 °C upon PL characteristics of He^+-implanted n-InP crystals is reported.

1. Introduction

Over the last years, the quality of InP single crystals has been considerably improved and now it is nearly at the level of GaAs quality. This success has been provided, on the one hand, by the reduction of residual impurity concentration in the crystals and, on the other hand, by generation or annihilation of host defects in a controlled manner. In particular, by employing the crystal annealing under phosphorus overpressure it has been established the possibility of preparing nominally undoped semiinsulating InP, the compensation mechanism being determined mainly by native defects [1 to 3]. Recently He^+ implantation in InP with subsequent annealing of samples was found to result in an improvement of crystalline quality in the near-surface layers [4]. It is to be noted that the increasing interest in radiation-induced defects in InP is caused, in particular, by some promising space applications of this material [5].

Although the luminescence related to ion-beam-induced defects in InP has been studied earlier (see, for instance, [6 to 8]), in most cases the implantation was followed by a post-implantation annealing at relatively high temperatures ($T_{ann} > 600$ °C). At the same time, little attention has been paid to the effect on PL of radiation defects (RD) which are stable at moderate temperatures ($T_{ann} < 600$ °C), including room temperature.

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The aim of this work is to present data concerning the peculiarities of PL in InP single crystals subjected to He^+ implantation with subsequent annealing at different temperatures in the interval 400 to 750 °C as well as in InP crystals and epilayers irradiated by high-energy α-particles.

2. Experimental

Nominally undoped (100)-oriented LEC-grown n-InP crystals (a) and VPE-grown layers (q) were used in this work. The electron concentration and mobility at $T = 300$ K in the as-grown single crystals were $n = 2 \times 10^{16}$ cm^{-3} and $\mu = 4.0 \times 10^3$ cm^2 V^{-1} s^{-1}, respectively. The epitaxial layers with a thickness of about 10 μm were grown by chloride–hydride deposition on semiinsulating InP:Fe substrates [9]. At $T = 77$ K, the electron density in the layers was $n = 2 \times 10^{14}$ cm^{-3} and the mobility was $\mu = 7.8 \times 10^4$ cm^2 V^{-1} s^{-1}.

100 keV He^+ implantation in LEC-grown InP single crystals was carried out at room temperature at a dose of 1×10^{15} cm^{-2}. During the implantation, the wafers were tilted to minimize channelling. According to TRIM simulations [10], in this case the projected ion range peak is centered at a depth of 0.54 μm. After implantation, the samples were annealed in an atmosphere of flowing hydrogen for 15 min at the following temperatures (b) 750, (c) 700, (d) 650, (e) 600, (f) 500, and (g) 400 °C. Non-implanted samples were annealed at temperatures 700 (c′) and 600 °C (e′) in order to discriminate between implantation and annealing effects. An InP proximity was used to avoid the surface decomposition during annealing.

We report the PL spectra at 4.2 K of the above samples as well as of both bulk crystals (h and i) and epitaxial layers (l, m, n, o, and p) subjected to 5 MeV α-particle irradiation at following doses: (i) 9×10^{12}, (h, m) 2.7×10^{12}, (n) 9×10^{11}, (o) 2.7×10^{11}, and (p) 9×10^{10} cm^{-2}. The α-irradiation was provided by a ^{238}Pu source.

A helium-flux optical cryostat (TBT-Alphagaz) allowed us to measure PL spectra at 4.2 K. The apparatus was equipped with a 25 mW He–Ne laser (NEC GLG5730), a Jobin Yvon HR640 monochromator, and a liquid-nitrogen-cooled germanium detector (North Coast E0817L). The signal-to-noise ratio was optimized by a vectorial lock-in (PAR 5209), and rejection of the cosmic ray noise was provided by a Muon Filter (North Coast 829B). The spectral resolution was 0.5 meV or less.

3. Results

3.1 He^+ implantation

Fig. 1 illustrates the PL spectra of the as-grown n-InP crystals as well as of the He^+-implanted ones after annealing at 750 and 650 °C. The spectrum of the as-grown samples consists of three bands with the maxima at 1.416, 1.374, and 1.333 eV. According to the literature data [11 to 13], the band at 1.416 eV is due to free- and bound-exciton recombination, while the one at 1.374 eV is connected with the radiative recombination of carriers via donor–acceptor (DA) pairs. The latter band is accompanied by a LO-phonon replica at 1.333 eV. The samples subjected to ion implantation and annealing exhibit lower PL intensities than the as-grown one which should be related to the combined effect of lattice recovery and concentration of radiative centers in the implanted layers. The effect of annealing on the intensity of DA luminescence in He^+-implanted n-

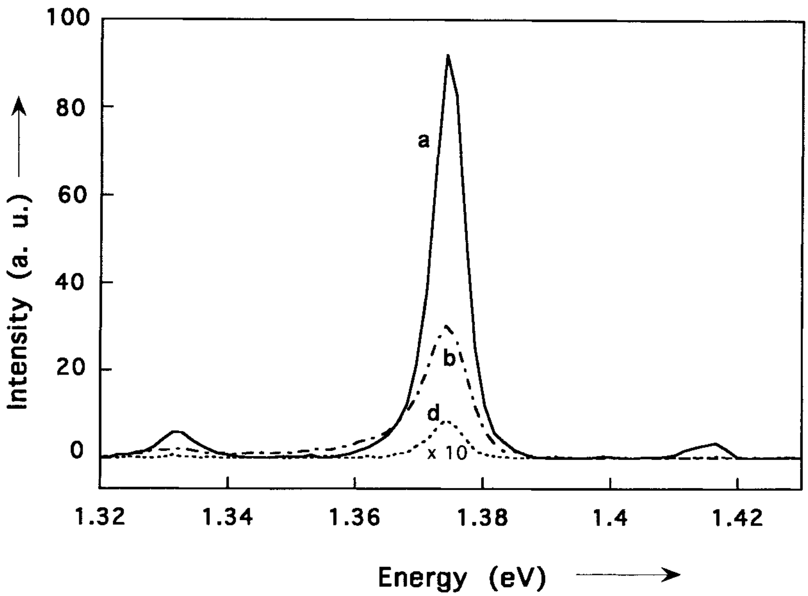

Fig. 1. PL spectra of as-grown LEC-InP crystals (a) and of He^+-implanted ones subjected to annealing at 750 (b) and 650 °C (d)

InP crystals is illustrated in Fig. 2. It is interesting to note that the broadening of the DA band does not depend significantly upon T_{ann}.

Now we shall consider the excitonic region of PL spectra.

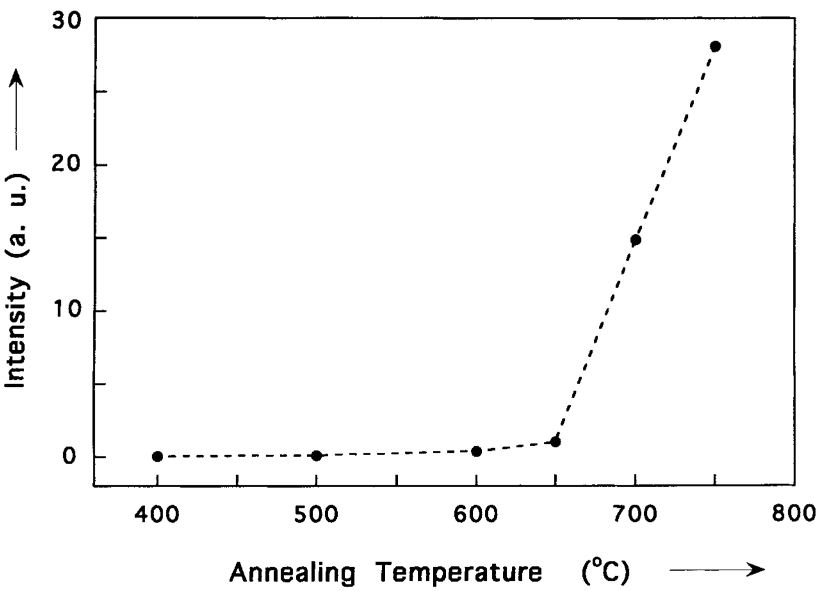

Fig. 2. Intensity of DA band at 1.374 eV vs. annealing temperature

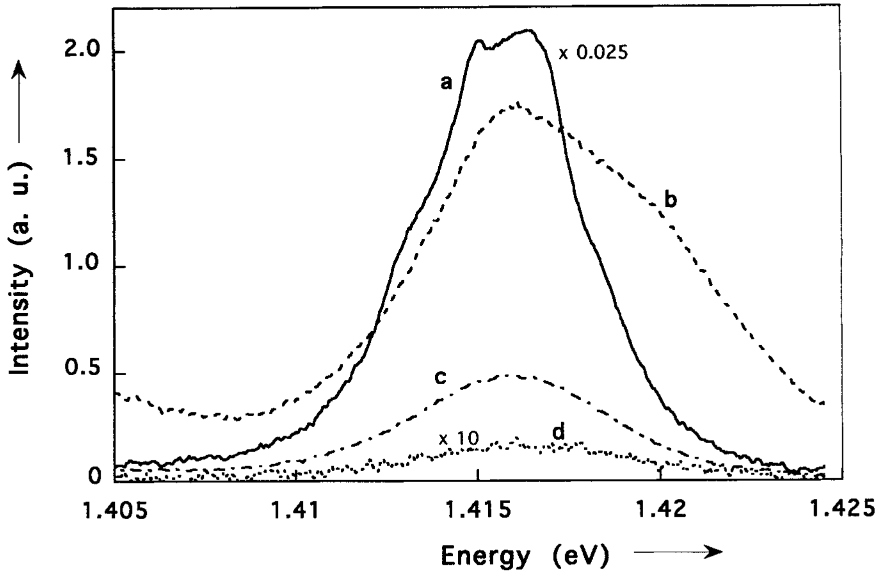

Fig. 3. Excitonic PL spectra of as-grown LEC-InP crystals (a) and of He^+-implanted ones. Temperature of post-implantation annealing: (b) 750, (c) 700, (d) 650 °C

The intensity of the excitonic peaks increases when the annealing temperature is raised (Fig. 3), so pointing to a recovery of the damaged lattice, even though it never reaches the intensity of the as-grown sample (a). Excitonic spectra of samples labelled (e), (f), and (g) are not reported because of their low intensity.

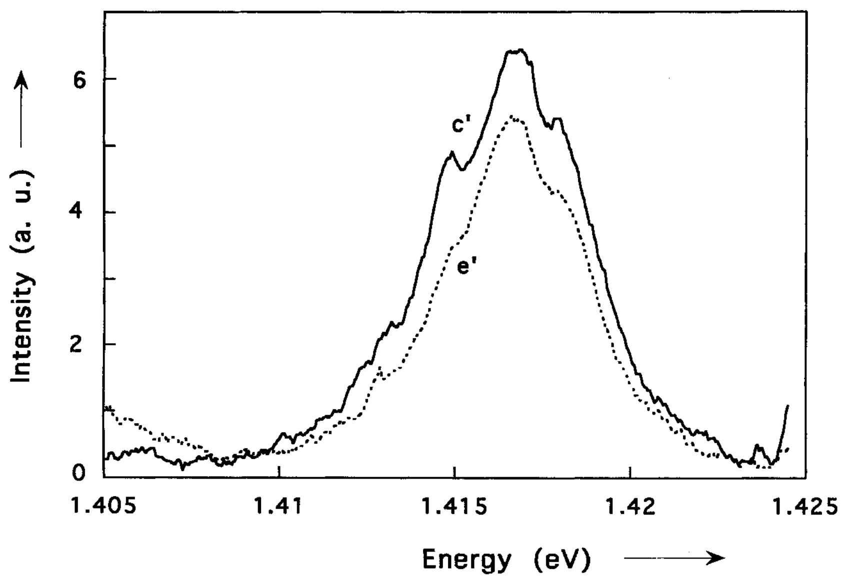

Fig. 4. Excitonic PL spectra of LEC-grown InP crystals annealed at 700 (c′) and 600 °C (e′)

In the excitonic region (Fig. 3), the spectrum of (a) exhibits two peaks of comparable intensity, centered at 1.4165 and 1.415 eV. These peaks are ascribed to radiative recombination of excitons bound to ionized donors (D^+, X) and neutral acceptors (A^0, X), respectively [12 to 14]. The high-energy shoulder is assigned to free-exciton (FE) recombination [15], while the low-energy tail may be attributed to neutral deep-donor bound-excitonic emission [14].

The analysis of the relative PL intensity in He^+-implanted samples shows that at high annealing temperatures the excitonic bands broaden and the FE peak relatively increases in intensity with respect to the bound-exciton ones. It is noteworthy that the increase in PL intensity with the annealing temperature is more pronounced for the non-excitonic peaks (see Fig. 2) than for the excitonic ones.

In case of non-implanted samples, the annealing gives rise to a relative increase of the intensity of FE and (D, X)-related bands with respect to other excitonic peaks (Fig. 4). As to the absolute intensity of excitonic luminescence in samples (c′) and (e′), it is about one order of magnitude less than in the as-grown crystals.

3.2 α-particle irradiation

At first we shall consider the effect of α-irradiation upon PL spectra of LEC-grown single crystals.

A diminution of PL intensity is observed in InP crystals with increasing dose of irradiation, this being more pronounced for excitonic transitions. In the excitonic region a redistribution of PL intensity may be noticed as well, namely, the intensity ratio between FE and bound excitons is higher in the irradiated samples compared with the as-grown one (Fig. 5).

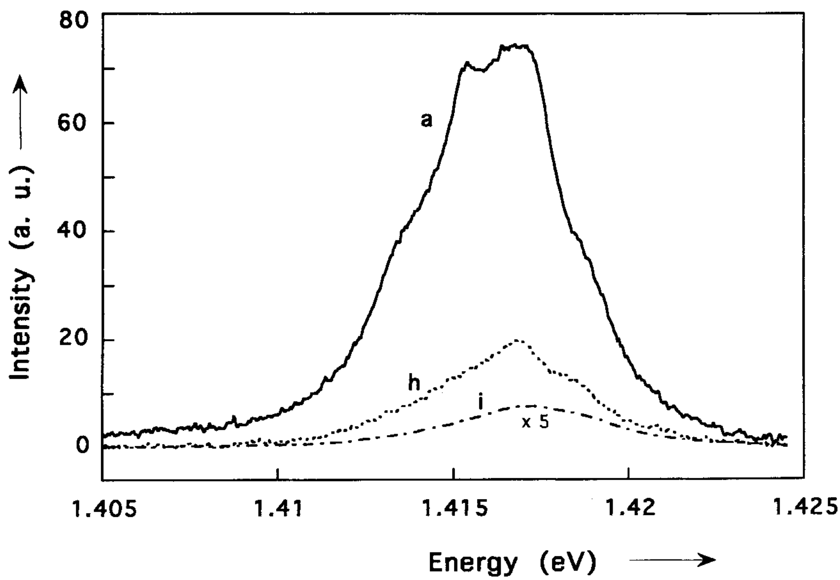

Fig. 5. Excitonic PL spectra of α-irradiated LEC-InP crystals. Dose of irradiation D: (a) 0, (i) 9×10^{12}, (h) $2.7 \times 10^{12}\ cm^{-2}$

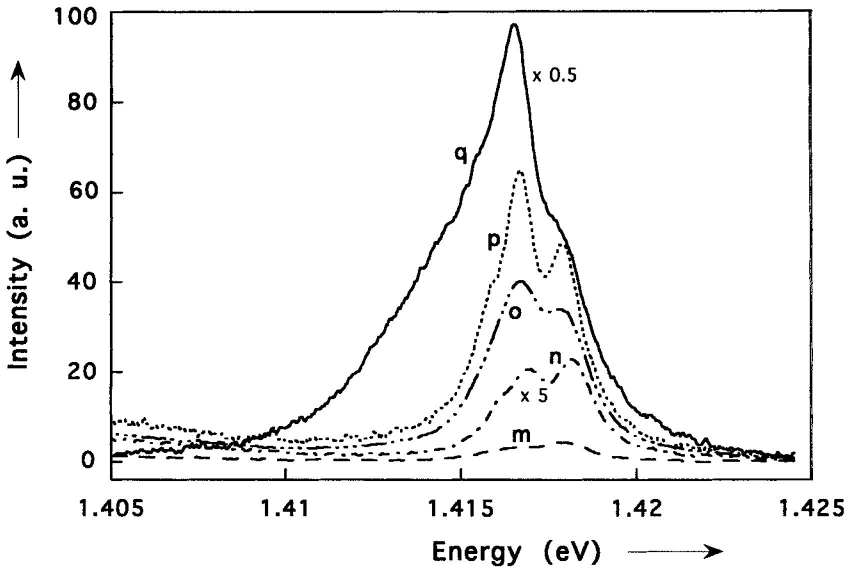

Fig. 6. Excitonic PL spectra of α-irradiated VPE-grown InP epilayers. Dose of irradiation D: (q) 0, (p) 9×10^{10}, (o) 2.7×10^{11}, (n) 9×10^{11}, (m) 2.7×10^{12} cm^{-2}

As to the DA peak at 1.374 eV, its energy position did not change after irradiation. For samples (h) and (i), the full width at half maximum (FWHM) of the band involved was found to be 7.5 meV, while that of the as-grown samples was about 7 meV. At the same time no new bands were observed after irradiation.

Let us pass now to α-irradiated VPE-grown epilayers.

The crystal quality of the as-grown epilayers, on the basis of good resolution of excitonic peaks and high intensity ratio between excitonic and non-excitonic luminescence (Fig. 6 and 7), proved to be better than that of LEC crystals. As is seen from Fig. 7, the excitonic PL spectrum of as-grown epilayers exhibits a strong peak at 1.4165 eV due to (D^+, X) recombination, and a shoulder at 1.4178 eV related to FE transitions. Both (A^0, X) and neutral deep-donor bound-excitonic emission seem to make a contribution to the low-energy tail of the excitonic PL spectrum [15].

We have found that, like in the previous series, the PL intensity diminishes with increasing the dose of irradiation, this effect being more pronounced for the excitonic region (Fig. 7). At the same time, one can note that the intensity decrease was more pronounced for bound-exciton recombination in comparison with that of FE recombination (Fig. 6). A deconvolution of the excitonic PL spectra was performed which did not evidence visible changes in the FWHM of the bands.

As regards the non-excitonic region, the spectrum of the as-grown sample (Fig. 7) represents a convolution of two peaks at 1.374 eV (band A) and 1.386 eV (band B), the A-band being more intense than the B-one. The α-irradiation of layers at the lowest dose (9×10^{10} cm^{-2}, sample (p)) leads to an increase in intensity of the B-band as well as to the appearance of a new peak C at 1.399 eV (Fig. 7). A weak PL peak was also evidenced at the energy 1.342 eV, which seems to be a LO-phonon replica of the B-band. Like the excitonic PL, the intensity of luminescence in the non-excitonic region was found to decrease with further rising of the dose of α-particles.

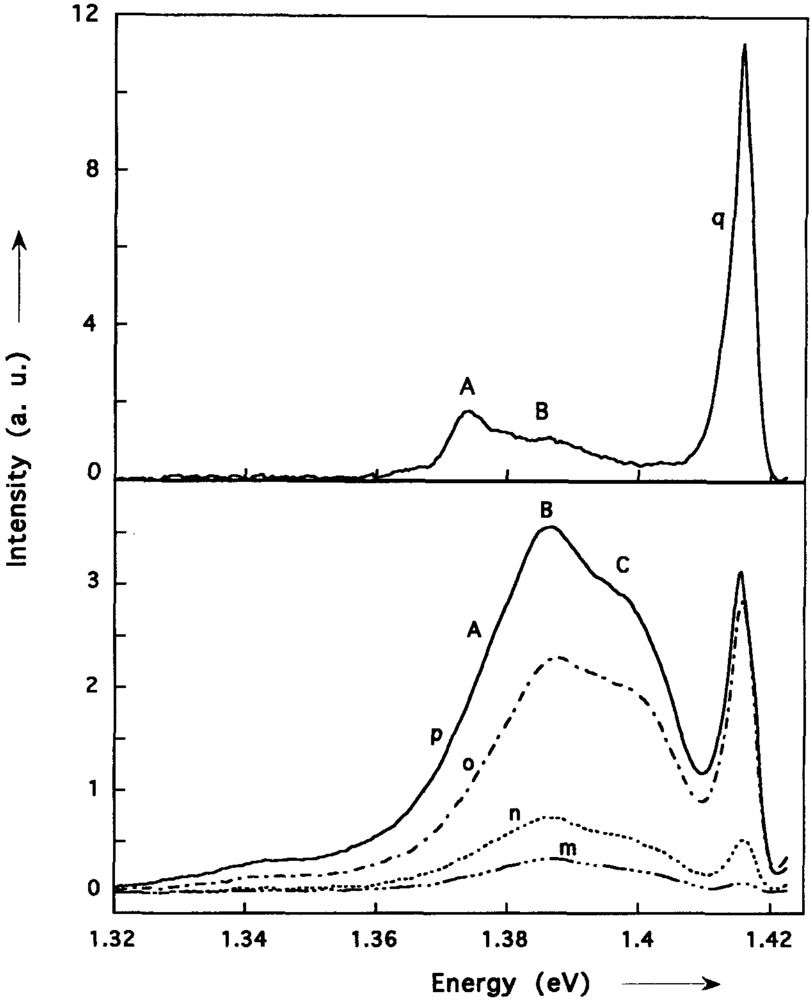

Fig. 7. PL spectra of α-irradiated VPE-grown InP epilayers. Dose of irradiation D: (q) 0, (p) 9×10^{10}, (o) 2.7×10^{11}, (n) 9×10^{11}, (m) 2.7×10^{12} cm^{-2}

4. Discussion

A high-energy particle impinging on matter loses energy through ionization of lattice atom electrons and through Rutherford scattering, the latter process producing lattice displacements, e.g., RD. Light ion bombardment is known to facilitate the energy deposition through electronic processes [16, 17]. In consequence of this, 100 keV He^+ implantation in InP at the dose of 10^{15} cm^{-2} does not result in the amorphization of the near-surface layer [4]. Taking this into account, both He^+ implantation and α-particle irradiation may be supposed to introduce in InP lattice defects without the formation of any amorphous phase.

When discussing the experimental results, we shall take into account the following processing-induced effects:

(i) generation during implantation and α-irradiation of lattice defects which may play the role of radiative recombination centers as well as of non-radiative ones;

(ii) interaction between different radiation defects as well as of residual impurities with RD leading to the formation of defect complexes;

(iii) changes in the defect concentrations caused by annealing of as-grown InP;

(iv) post-implantation annealing of RD.

The decrease of integral PL intensity observed after He^+ implantation and α-irradiation may be attributed to the creation of non-radiative recombination centers competing with the radiative recombination ones in the capture of photogenerated carriers. As it has been mentioned above, the decrease in PL intensity with rising α-fluence is more pronounced for bound-excitonic recombination than for FE emission (see Fig. 3 and 6). Similar behaviour of excitonic PL bands was observed recently in 4 MeV electron-irradiated InP epilayers [18]. According to [9, 18], the effect under consideration is a consequence of decreasing density of isolated residual impurity atoms due to their interaction with RD.

As it is seen from Fig. 4, annealing of as-grown crystals at 600 to 700 °C also increases the ratio between free- and bound-excitonic PL intensities. One can note, in this regard, that InP single crystals have been found to contain shallow non-equilibrium (e.g., frozen) donors. Thermal treatment of LEC-grown samples at 600 to 700 °C leads to the annealing of such donors and, as a consequence, to a decrease in free-electron concentration [2, 13]. We have annealed bulk InP crystals at 650 °C for 96 h. After annealing the electrical parameters at $T = 300$ K were the following: $n = 4.3 \times 10^{15}$ cm^{-3} and $\mu = 4.2 \times 10^3$ cm^2 V^{-1} s^{-1}. Although at present it is difficult to find a relationship between changes in excitonic PL intensity and reduction of concentration of shallow donors, these phenomena are indicative of a rather strong dependence of the densities of lattice defects upon the temperature of sample processing.

The increase in PL intensity in He^+-implanted crystals with rising T_{ann} (Fig. 2) seems to be caused mainly by the annealing of RD. The PL data, however, do not show an improvement of the crystalline quality like that evidenced earlier by Raman scattering measurements in samples subjected to He^+ implantation with subsequent annealing at 600 to 700 °C [4]. In order to explain this difference one has to take into account the influence of surface on PL intensity in our experiments. Indeed, since the energy of the laser quanta $h\nu \gg E_g$, the non-equilibrium carriers are generated in the near-surface layer with a thickness of some hundreds of nanometers, which implies an intense non-radiative recombination of carriers through the surface states.

Let us discuss now the peculiarities of non-excitonic bands observed in n-InP epilayers (Fig. 7). At least two PL bands, namely B and C, exhibit an increase in intensity when the layers are irradiated by α-particles at the dose 9×10^{10} cm^{-2}. Consequently, the bands involved may be related to host lattice defects. One can note, in this regard, that new PL bands close in energy with the B and C ones were observed recently in 4 MeV electron-irradiated n-InP epilayers [19, 20]. One of them, centered at 1.390 eV, was attributed to the In_P antisite. Since MeV-energy α-particles possess relatively large defect introduction rates in InP [21], defect complexes rather than isolated point defects may be expected to prevail in the irradiated samples. According to [22], the energy of quanta emitted through free-to-bound electron transitions increases if an acceptor center like In_P interacts with a shallow donor D to form defect complexes. Taking this into consideration, the PL band at 1.399 eV may be connected with $[In_P, D]$ complexes. For the purpose of comparison, one can notice that a similar PL band with the maximum at 1.401 to 1.403 eV ($T = 2$ K) was earlier observed [8] in high-purity InP single crystals and attributed to acceptor-like complexes. Moreover, the intensity of that band was established to increase after low-dose Ar^+ implantation. This result, in our opinion, is also indicative of the host–defect nature of the corresponding radiative centers.

5. Conclusions

As in 4 MeV electron-irradiated InP [18], the evolution of bound-excitonic PL spectra after He^+ implantation and α-irradiation of samples proved the interaction of shallow residual impurities with RD. Unlike Raman scattering measurements [4], no improvement of the crystalline quality has been evidenced by PL analysis of n-InP single crystals subjected to He^+ implantation with subsequent annealing at 600 to 700 °C. This discrepancy was explained taking into account the non-radiative recombination of free carriers through the surface states.

The new bands observed in α-irradiated n-InP epilayers at 1.386 and 1.399 eV have been ascribed to lattice defects, the latter being connected with defect complexes involving In_P antisites. In order to get better understanding of the nature of luminescence in this region, a PL characterization as a function of sample temperature and density of excitation power is now in progress in our laboratories.

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