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IMPROVEMENT OF InP CRYSTALLINE PERFECTION BY He^+-IMPLANTATION AND SUBSEQUENT ANNEALING

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The influence has been studied of 100-keV He^+-ion implantation and subsequent thermal annealing on Raman scattering spectra of LEC-grown InP single crystals with (1 0 0)- and (1 1 1)-crystallographic orientations of the surface. Improvement of InP crystalline perfection was observed after He^+-implantation at the dose $1 \times 10^{15}\,cm^{-2}$ followed by sample annealing at 600–700°C. Implant-induced removal of thermally stable defect clusters related with the growth process is supposed to be primarily responsible for the phenomenon involved.

Keywords: A. semiconductors, D. order–disorder effects, D. radiation effects, E. inelastic light scattering.

INDIUM PHOSPHIDE is an important material for optoelectronic and high frequency microelectronic devices. In a rather short period of time (about 5 years) the quality of InP bulk single crystals has been considerably improved and now it is nearly at the level of gallium arsenide quality [1]. In particular, it was established the possibility of preparing nominally undoped semi-insulating InP by crystal annealing under phosphorus overpressure [2–4]. On the other hand, better understanding of radiation-related processes in InP was achieved. Implant-induced host defects have been shown to contribute mainly to the enhancement of *n*-type conductivity [5, 6] thus impeding the formation of high-resistivity layers as well as the effective activation of ion-implanted acceptor impurities [7].

For the purpose of studying lattice imperfections in ion-implanted layers resonant Raman scattering (RS) can be used [8]. This method was successfully employed for the investigation of lattice disorder in InP single crystals caused by the implantation of impurities such as Be^+, Mg^+ and Ga^+ [9–12]. It was established a gradual disordering of the lattice with increasing the dose of implantation [9–11] as well as the formation of a new material consisting of In, P and Mg in the case of Mg^+-implantation at high doses [12]. In order to get new information about the peculiarities of processing-induced order–disorder phenomena in InP, we studied RS spectra in He^+-implanted indium phosphide single crystals before and after post-implantation annealing. An improvement of the crystalline quality was evidenced under certain conditions of sample processing.

(1 0 0)- and (1 1 1)-oriented wafers sawed from nominally undoped LEC-grown *n*-InP ingots were investigated. Electron concentration and carrier mobility at $T = 300\,K$ in as-grown single crystals were $2 \times 10^{16}\,cm^{-3}$ and $4.0 \times 10^3\,cm^2\,V^{-1}\,s^{-1}$, correspondingly. After mechanical polishing and chemical etching in Br_2-methanol solution the wafers have been subjected to implantation by 100-keV He^+-ions at different doses from 1×10^{13} to $1 \times 10^{15}\,cm^{-2}$. Ion implantation was carried out at sample temperatures of about 30°C, the wafers being tilted to minimize channelling. According to TRIM (transport of ions in matter) simulations [13], in this case the projected ion range peak is centered at a depth of $0.54\,\mu m$. After implantation, sections from the wafers were annealed in a hydrogen atmosphere for 15 min at temperatures between 400 and 700°C. To avoid thermal decomposition of the sample surface an InP proximity was used, e.g., the role of protective cap was played by an as-grown InP wafer. Unpolarized Stokes-component RS spectra have been measured at room temperature in a quasi-backscattering geometry by an automatic set-up based on a double DFS-52

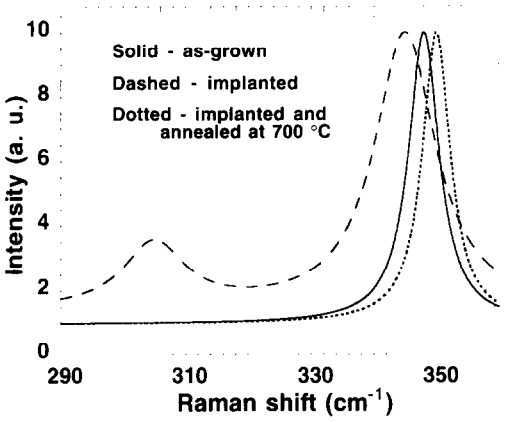

Fig. 1. Normalized RS spectra of (1 0 0)-oriented InP before and after processing. The dose of He^+-implantation equals 1×10^{15} cm^{-2}.

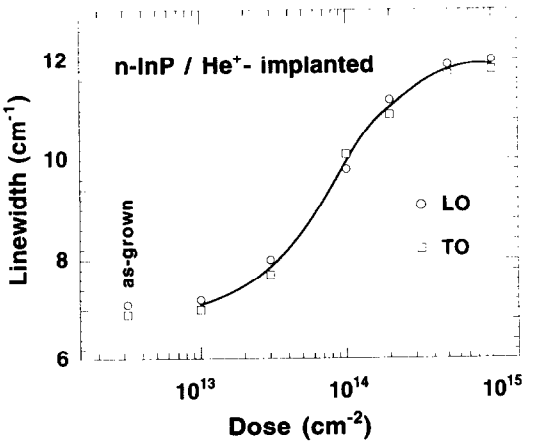

Fig. 3. Dependence of the RS band width upon implantation dose for (1 1 1)-oriented InP samples.

spectrometer with the spectral resolution better than 1 cm^{-1}. The excitation was provided by the 532-nm line (200 mW) from a solid-state laser. At this wavelength the penetration depth of the light in InP samples is comparable to the penetration depth of the implanted ions. The diameter of the focused laser beam in the crystal was about 0.1 mm. A FEU-79 photomultiplier was used in the quantum counter regime.

RS spectra of as-grown InP crystals are shown in Figs. 1 and 2. A single RS band centered at 348 cm^{-1} is observed in (1 0 0)-oriented as-grown InP wafers while the RS spectrum of (1 1 1)-oriented wafers consists of two bands with the maxima at 348 and 308 cm^{-1}. These first-order scattering bands are connected to Brillouin-zone-center ($\mathbf{q} = 0$) LO- and TO-phonons, respectively. According to the selection rules for InP-type crystal structure [9], both phonons under consideration are allowed in the (1 1 1)-backscattering geometry. At the same time the RS at Brillouin-zone-center TO-phonon is forbidden in (1 0 0)-geometry, which is in full agreement with the observed data.

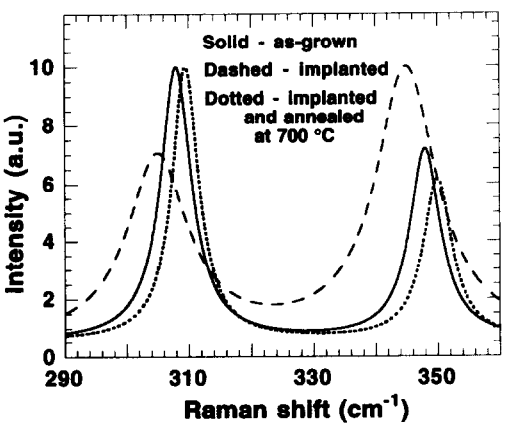

Fig. 2. Normalized RS spectra of (1 1 1)-oriented InP before and after processing. The dose of He^+-implantation equals 1×10^{15} cm^{-2}.

After He^+-implantation the RS bands were found to gradually broaden and shift towards the low frequencies with the fluence rise (Figs. 1–3). It is important to note that the increase of He^+-fluence up to 10^{15} cm^{-2} leads to the appearance in the (1 0 0)-geometry RS spectrum of the TO-mode, forbidden in the configuration involved (Fig. 1, dashed curve). Similar effect was observed earlier [9–12] and attributed to the breakdown of the selection rules caused by the disorder-induced destruction of the quasimomentum conservation.

As distinct from [10, 11], we observed the same broadening with the increase of the ion fluence for both LO- and TO-phonon-related RS bands (Fig. 3). According to [8], the RS band broadening reflects the accumulation of lattice defects during the implantation. It is interesting to note that in the case of He^+-implantation the broadening curves tend to saturation when the ion fluence approaches 10^{15} cm^{-2} (see Fig. 3; an analogous behaviour was observed when analysing the dependence of the energy position of RS band maxima upon the ion fluence). This effect cannot be attributed to the formation of an amorphous layer since no RS bands inherent to amorphous InP [9, 10] have been observed by us. In our opinion the saturation in the amount of disorder may be a manifestation of dynamic annealing of defects occurring during He^+-implantation in InP. One can notice that the dynamic annealing of radiation defects was evidenced earlier in Si^+-implanted GaAs [14].

In order to study the process of the crystal lattice recovery, measurements of RS spectra were performed on InP samples subjected to implantation at the highest dose (1×10^{15} cm^{-2}) with subsequent

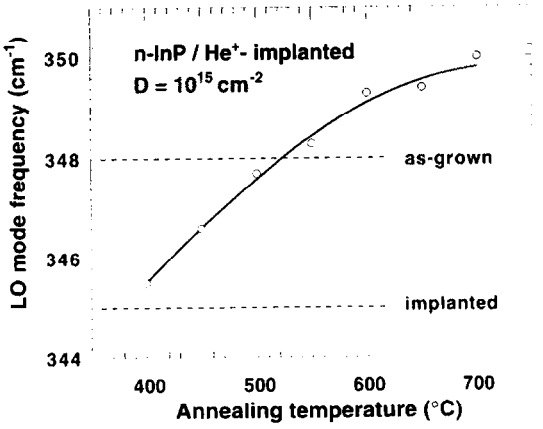

Fig. 4. Dependence of the frequency of LO-phonon-related RS band maximum upon the post-implantation annealing temperature for (1 1 1)-oriented InP samples.

annealing. The crystal lattice was found to recover with increasing T_{ann} and the RS spectra after the sample annealing at 550°C practically coincided with the ones for the as-grown crystals. Further increase of T_{ann} resulted in a shorter wavelength shift of the RS band maxima in comparison with the energy position of the bands in the as-grown crystals (Fig. 4). Even some narrowing of the RS bands can be noticed after sample annealing at 700°C (Figs. 1 and 2, dotted curves). These effects, obviously related with the increase in coherence length of the optical phonon modes [8], are indicative of an improvement of crystalline quality in the near-surface region of InP.

The phenomenon involved can be explained as follows. The as-grown InP single crystals may contain different precipitates and defect clusters related with the growth process [15, 16] which are stable at usual temperatures of post-implantation annealing (700–740°C [12]). Implantation of 100-keV He^+-ions at the dose $10^{15}\,cm^{-2}$ causes the lattice disorder which appears to be accompanied by fast diffusion of defects and their dynamic annealing. Under such conditions a removal of thermally stable defect clusters and precipitates may take place. In consequence of this, the post-implantation annealing at 600–700°C gives rise to a new lattice which proves to be more perfect in comparison with the lattice of the as-grown samples. It is to be noted that similar phenomenon was recently observed in GaAs epilayers subjected to Si^+-implantation and subsequent annealing [17].

The improvement of crystalline perfection has been observed only on He^+-implanted side of InP wafers. Taking this feature into account one can conclude that the crystalline quality may be improved providing that (a) the crystal lattice is heavily-damaged by He^+-ion implantation, this process being accompanied by a destruction of thermally stable defect clusters, and (b) the annealing of the implanted layers takes place at 600–700°C. At the same time we cannot exclude the contribution of other mechanisms to the lattice perfection improvement. For example, during implantation and annealing a radiation-stimulated out-diffusion of residual impurities may occur resulting in a purification of the near-surface InP layer.

Thus, He^+-ion implantation with subsequent annealing proves to be useful for the purpose of improving the crystalline quality of InP near-surface layers. This may be of peculiar importance for InP-based homo- and heteroepitaxial technology. In order to get a better understanding of the order–disorder processes in the He^+-implanted layers a photoluminescent spectroscopic study is now in progress. The results will be described elsewhere.

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