grown $Zn_{1-x}Fe_xSe$ ($0 \leqslant x \leqslant 0.22$). Fe is the minority element in the sample and the Fe edge data have larger statistical errors than the Zn edge data. As a result, the uncertainty in the Fe-Se distance is too large to allow any useful conclusion.

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Retardation of implantation damage annealing in InP due to local nonstoichiometry

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The regrowth of P- or Si-implanted InP following thermal annealing (400–600 °C, 2–20 h) has been studied using Rutherford backscattering channeling experiments. Differences in damage annealing are consistently found between identically treated ^{29}Si- or ^{31}P-implanted regions on the same sample, the former always being retarded. This retardation is suggested to be caused by stoichiometric imbalance due to the recoil kinematics, which is less severe for the case of the phosphorus implantation.

Ion implantation into InP is an area of growing interest because of the potential use of that material for microelectronic and electro-optical devices.[1,2] In order to obtain the desired electrical activity, the implantation must be followed by an effective annealing procedure. This annealing must restore the crystallinity, place the implants on proper lattice sites (as is the case for single-elemental semiconductors) and, for compound semiconductors, it must also restore the exact stoichiometry down to the atomic scale. In compound semiconductors a stoichiometric imbalance may be caused by the recoil energy imparted by the implanted ion to the constituent atoms. This will be particularly noticeable in crystals containing atoms that differ greatly in mass, as is the case for InP, which is composed of atoms differing in mass by nearly a factor of 4 ($m_P = 31$, $m_{In} = 115$); (in that respect InP differs greatly from GaAs, where the constituents are of nearly equal mass). Calculations of mean stoichiometric imbalance that employ the Boltzmann transport equation[3] have shown[4] (Fig. 1) that an imbalance in stoichiometry should result from the implantation of Si into InP, leaving the near-surface region phosphorus poor and the region beyond the projected range of the implants with an excess of P. In the present work we show that this imbalance has a detrimental effect on the annealing of Si-implanted InP. By comparing the annealing of ^{29}Si- and ^{31}P-implanted InP, for which the P recoil profiles are rather similar, with the only difference that the P-implanted sample contains more phosphorus, we could clearly demonstrate the importance of stoichiometric imbalance in the annealing behavior of compound crystals.

Semi-insulating (Fe-doped) ⟨100⟩ InP crystals were used in the present study. The samples were implanted with 180-keV $^{31}P^+$ or $^{29}Si^+$ ions to a dose of 1×10^{15} cm^{-2}. In order to obtain complete amorphization and to minimize self-annealing, all implantations were performed at liquid-nitrogen temperatures keeping the beam current density below 1 μA/cm.^{2} Both Si and P implantations were carried out on different parts of the same specimen to ensure identical processing. An unimplanted region was left on each sample for process control. Annealing was performed on SiO_2 encapsulated samples at 400, 500, and 600 °C for 2, 10, and 20 h in a conventional open tube furnace under a flow of N_2 gas. The caps were removed after the annealing by dipping in buffered HF followed by proper rinsing.

The implantation damage and its changes as a result of the annealing were deduced from Rutherford backscattering (RBS) channeling experiments using 0.9-MeV He^+ beams. From such experiments, information about the nature, amount, and depth distribution of irradiation-induced damage in single crystals, can be deduced.[5] Figure 2(a) shows

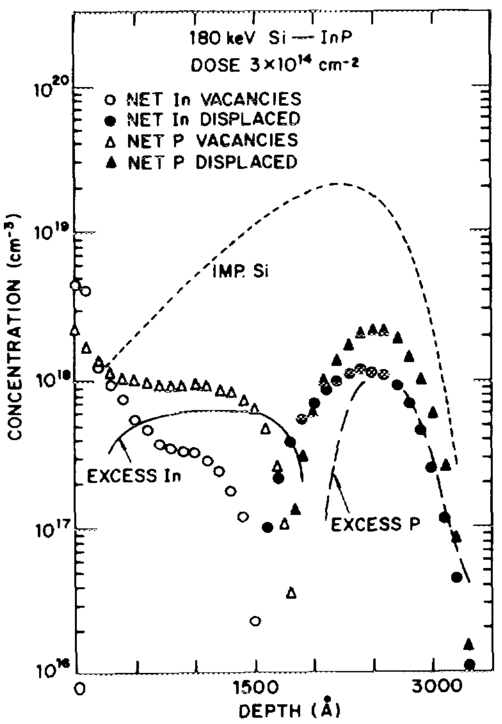

FIG. 1. Boltzmann transport equation calculation of stoichiometry distribution for Si-implanted InP (3×10^{14} cm^{-2}, 180 keV) (from Ref. 9).

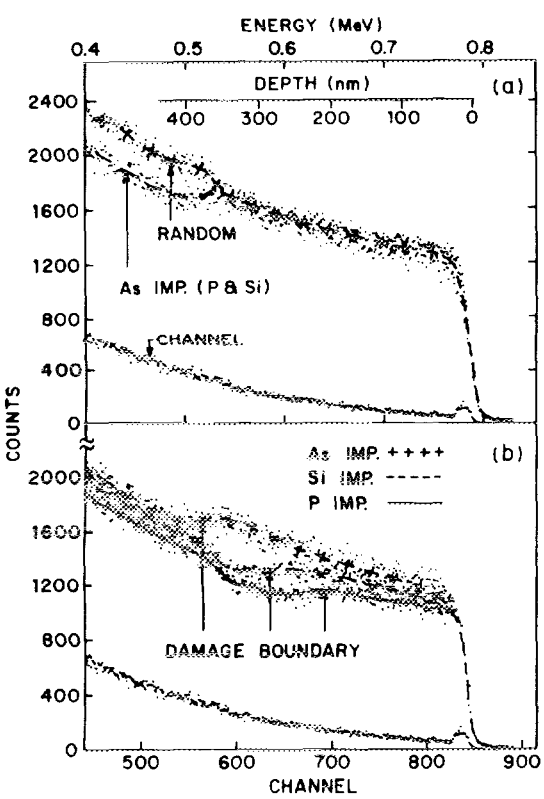

FIG. 2. Channeling RBS spectra for ^{31}P and ^{29}Si-implanted (180 keV, 1×10^{15} cm^{-2}) InP. (a) Unimplanted (channel and random) and as-implanted (P or Si implantations). (b) after annealing (500 °C, 10 h).

typical RBS spectra taken with the probing beam aligned along ⟨100⟩ and a random direction for the unimplanted (virgin) as well as the Si- and P- implanted parts of the same sample. Both Si- and P- implanted channeling spectra are indistinguishable, showing an amorphous layer 3850 Å thick. The channeled RBS spectra obtained for this sample after annealing at 500 °C for 10 h are shown in Fig. 2(b). The following points can be noted:

(i) The annealing has led, for both implants, to some narrowing of the damage peak accompanied by a decrease in damage peak height.

(ii) The above effects are more pronounced for the P-implanted section of the sample than for the Si-implanted one.

A similar behavior was noticed for all other annealing procedures employed and has been verified in repeated experiments carried out for confirmation. The narrowing of the damage peak width indicates that some epitaxial regrowth (shrinkage of the damage region) accompanied by a reduction in the density of backscattering centers in that region (decrease of the damage peak height) has occurred. Both these phenomena indicate that some annealing and damage rearrangement have resulted from the thermal treatment. These become more pronounced when longer annealing times or higher annealing temperatures are employed, and they are always more pronounced for the P- than the Si-implanted parts.

In order to obtain quantitative results, the measured RBS spectra were fitted to smooth curves composed of several fourth-degree polynomials. The derivative of these curves was taken so that the inflection points that reflect the boundary between the damaged and underlying crystalline region could be accurately determined. The shrinkage of the damaged region could thus be deduced for each annealing time and temperature for both P and Si implantations. The regrowth thicknesses obtained in that way are plotted against the inverse annealing temperature in Fig. 3; the lines represent least-square fits through the points.

The results summarized in Fig. 3 lead to the following interesting conclusions. The regrowth of InP, when implanted with Si ions, is consistently lower than that of identically treated P implantations, both, however, being slow . Nevertheless, the regrowth in both cases is governed by very similar low activation energies. The activation energies deduced from all six lines shown in Fig. 3 have rather similar slopes, corresponding to activation energies between 0.10 and 0.15 eV. These energies are lower by about a factor of 10 than the regrowth activation energies measured by Licoppe and coworkers[6] for the annealing of As-implanted thin amorphous layers (800 Å) of InP heated to 220–340 °C for just a few minutes. In that work regrowth rates as high as 300 Å/s were measured at 340 °C and complete damage removal could be obtained. The contradiction between the annealing behaviour of implanted InP of Licoppe *et al.* and of the present work can be explained by the difference in the initial amorphous layer thickness. It has been shown[7–9] that there exists a critical thickness beyond which amorphous layers of InP and other III-V crystals cannot be completely recrystallized. The thickness of the damaged layer in the present work

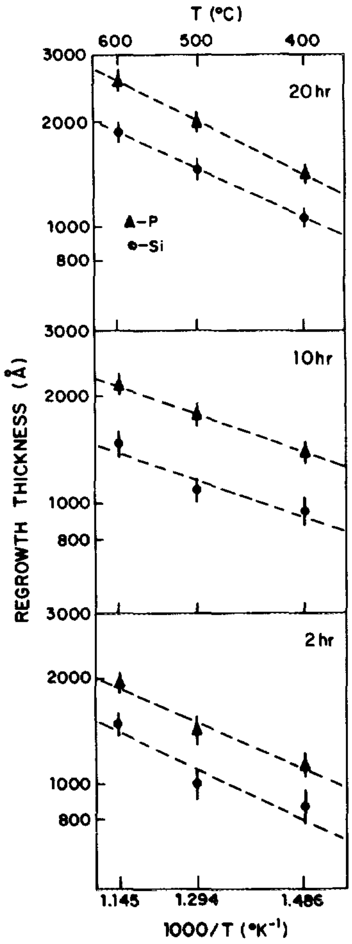

FIG. 3. Regrowth thickness vs annealing temperature of the implantation amorphized layer following annealing for 2, 10, and 20 h.

(3850 Å) is well above this critical thickness (~2000 Å), whereas that of the work of Ref. 6 (800 Å) was below it. Furthermore, the temperature range employed here (400–600 °C) was higher than that of Ref. 6, hence it is conceivable that a different annealing regime has been probed in the present work. The functional dependence of the damage peak shrinkage on time, which fits the present data, follows roughly a $t^{0.1}$ behavior; however, the curves fitted to that function do not pass through the origin. Hence a rapid annealing stage must have preceded the annealing regime probed here. This unobserved transient fast annealing may well correspond to the low-temperature region addressed by Licoppe *et al.*,[6] however, due to the large thickness of the damaged layer of the present work this annealing could not completely remove the damage nor affect significantly the damage shrinkage. The present observation that the damage peak has reduced in height only a little as a result of the annealing indicates that the damaged region has reconstructed into a structure that shows up in the channeling RBS spectra as a reduced damage peak, such as expected for a layer of slightly misoriented crystallites.

The lack of P in the damage region seems to both inhibit the regrowth of the damage region and to reduce the size of the crystallites leading to a higher and broader damage peak. The solid-phase epitaxy is apparently limited by the bulk diffusion of the In and P atoms. Fast epitaxial regrowth is only possible when the constituent elements are available in the correct proportions near the interface between the damaged and recrystallized regions. Since the self-diffusion coefficients of In and P in InP are drastically different [10^{-13} and 3×10^{-16} cm^2/s for In and P, respectively, at 750 °C (Ref. 10)], the successful reordering of nonstoichiometric InP is limited by the arrival rate at the interface of the slowly diffusing P. This is facilitated in the present experiment by P implantation as compared to Si implantation, which leads to the better regrowth of the former. At those distances where stoichiometric imbalance can not be restored quickly enough, small crystallites of the correct composition form, with the grain boundaries serving as sinks for the nonstoichiometric defects (presumably P vacancies). This process is more pronounced for the more P-deficient case of the Si implantation. Hence the higher damage peak is observed for the Si-implanted part on the sample as compared to the P-implanted one.

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