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Ultrafast carrier trapping and recombination in highly resistive ion implanted InP

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MeV P⁺ implanted and annealed p-InP, and Fe⁺ implanted and annealed semi-insulating InP have both been shown to produce the high resistivity, good mobility, and ultrafast optical response desired for ultrafast photodetectors. Hall effect measurements and time resolved photoluminescence were used to analyze the electrical and optical features of such implanted materials. Low temperature annealing was found to yield the fastest response times—130 fs for Fe⁺ implanted and 400 fs for P⁺ implanted InP, as well as resistivities of the order ~10⁶ Ω/square. It was found that the electrical activation of Fe-related centers, useful for achieving high resistivities in Fe⁺ implanted semi-insulating InP, was not fully realized at the annealing temperatures chosen to produce the fastest optical response.Implanting p-InP in the dose regime where type conversion occurs, and subsequent annealing at 500 °C, produces high resistivities and ultrafast carrier trapping times that are only marginally dose dependent. © 2003 American Institute of Physics.

I. INTRODUCTION

Semiconductor materials with high resistivity, good electron mobility, large breakdown fields, and fast optical response are essential for a variety of applications, including ultrafast photodetectors, optoelectronic and all-optical switches, and saturable absorbers. GaAs grown by molecular beam epitaxy at low substrate temperatures (LT GaAs), a material with a complete combination of these characteristics, was grown in 1988.1–3 Subsequently, similar characteristics were discovered in ion-implanted GaAs.4 Investigations progressed towards InP as well. LT InP was grown in 1992,5 but the resulting layers were highly conductive (n-type) due to the ionized level of the phosphorus antisite defect which lies in the conduction band, making the material unsuitable for optoelectronic applications.6 Additional studies of As⁺ and P⁺ implantation into semi-insulating (SI) InP have shown that the defects introduced by implantation and annealing are of shallow donor type, leading to low resistivities.7 However, by implanting into p-InP layers in the dose range of 1×10¹⁴–1×10¹⁵ cm⁻², where a carrier type change takes place, the sheet resistance could be raised to values as high as 10⁵ Ω/square. In this article, we report a thorough analysis of P⁺-implanted InP for the dose regime under which type conversion takes place in p-InP. Moreover, as a possible alternative, we investigate InP implanted with Fe⁺ ions. Fe-doped InP is widely used for current blocking layers in electronic and optoelectronic devices, since Fe²⁺/³⁺ states are located close to the midgap and ensure SI properties of the material. However, the concentration of Fe traps in Fe-doped InP is limited by Fe precipitation, and carrier trapping times shorter than 10 ps can barely be achieved.8

Thorough electrical and time-resolved optical measurements performed in the present work have allowed us to pinpoint the optimal implantation and annealing regimes to achieve materials best suited for optoelectronic applications. Additionally, analysis of the experimental results has indicated which defects are mainly responsible for the electrical properties and ultrafast carrier trapping and recombination. Finally, a comparison of materials obtained by the two different methods has made it possible to evaluate them in terms of applicability in devices.

II. SAMPLE PREPARATION AND CHARACTERIZATION

Semi-insulating (100) InP wafers were implanted with 2 MeV Fe⁺ ions at 200 °C and a dose of 1×10¹⁴ cm⁻² and then annealed at temperatures between 500 and 900 °C for 30 s. Additionally, a 1.5-μm thick p-InP (p~1.3×10¹⁸ cm⁻³) layer was grown on a similar semi-insulating (100) InP substrate, implanted at 200 °C with 1 MeV P⁺ ions at doses between 1×10¹⁴ and 1×10¹⁵ cm⁻² and also annealed at 500 and 600 °C. According to transport of ions in matter (TRIM) simulations, the ion energies chosen for this work would place the peak damage at 1 μm from the surface. Hall effect measurements were carried out using the van der Pauw geometry, with indium metal ohmic contacts.

Carrier dynamics in implanted InP samples have been studied by time-resolved photoluminescence (PL). Measurements were performed at room temperature using an upconversion setup based on a self-mode-locking Ti:sapphire
laser (80 fs, 95 MHz, 770 nm). The average excitation intensity was between 1 and 100 mW, a spot diameter ~20 μm. Taking into account reflection losses and averaging over one absorption length, this corresponds to a photoexcited carrier density between $1.1 \times 10^{17}$ and $1.1 \times 10^{19}$ cm$^{-3}$, respectively. The temporal resolution of the measurements was 130 fs. The PL transients were measured within a spectral window of 20 nm centered at the band gap wavelength of 920 nm.

III. RESULTS AND DISCUSSION

A. Electrical properties

Figure 1 shows Hall effect measurements carried out on p-type InP implanted with 1 MeV P$^+$ ions and annealed at 500 and 600 °C, respectively. For annealing at 500 °C, the sheet resistance $R_s$ at a dose of $5 \times 10^{14}$ cm$^{-2}$ is smaller for annealing temperatures greater than that produced by P$^+$ ions and annealed at 500 and 600 °C, respectively. The samples probably have a layer of implanted samples is nonuniform, and it is more than likely that several layers with different conductivity are present. The samples probably have a layer of implanted samples, multiple conductivity layers are expected due to the nonuniform distribution of the defect profiles.

Hall effect measurements on 2 MeV Fe$^+$ implanted SI InP over a range of doses (not shown) have shown that the maximum sheet resistance ($\sim 10^6$ Ω/square) for an unannealed sample is obtained for a dose of $1 \times 10^{14}$ cm$^{-2}$. For implantation at a dose of $1 \times 10^{15}$ cm$^{-2}$, the sheet resistance is reduced to $\sim 3 \times 10^5$ Ω/square, showing that the electrical properties of InP implanted with Fe$^+$ have a strong dose dependence. Below, we concentrate on the dose of $1 \times 10^{14}$ cm$^{-2}$ and study electrical parameters for various annealing temperatures.

Figure 2 shows the corresponding Hall effect results for annealing of Fe$^+$ implanted InP up to 900 °C. Without annealing, the sample is n-type, and $R_s$ is very high, at $\sim 10^6$ Ω/square. Increasing the annealing temperature causes $R_s$ to decrease, until at 600–700 °C the conductivity changes to p-type. The sheet carrier concentration, $C_s$, at low annealing temperatures is greater than that produced by P$^+$ implantation by approximately an order of magnitude. This can be explained by a higher concentration of defect-related donors introduced by implantation with an ion of larger atomic mass. For annealing at 600 and 700 °C, $C_s$ reaches a maximum of $1.2 \times 10^{12}$ cm$^{-2}$.
B. Optical characterization

Time-resolved PL measurements provide information on the rate of carrier trapping into deep centers and, under certain experimental conditions, of carrier recombination. In combination with the electrical properties, they also allow us some insight into the origin of active traps.

Figure 3 shows PL transients for the Fe⁺-implanted InP, for different annealing temperatures. On the time scale of interest, the temporal changes in electron and hole concentrations occur mainly due to carrier trapping, because radiative recombination is a much slower process and occurs in nanoseconds. As one can see from Fig. 3, even though the implantation dose for all the samples is the same, the PL transients are very different. This indicates that the PL dynamics is determined by photoexcited carrier trapping to implantation and/or annealing induced defects rather than Fe-related defects (possibly Fe⁺/Fe²⁺ centers), which, otherwise, are efficient carrier recombination centers with similar electron and hole trapping rates. The PL decay times, extracted from the exponential fits to the PL transients, are in the range from 130 fs to 46 ps for the samples annealed at 500 and 900 °C, respectively. For the 500 °C sample, the decay time was obtained after initial deconvolution of the PL transient with the pulse cross-correlation trace. No signal could be obtained for the unannealed sample for which the decay time is probably even shorter.

For all the Fe-implanted samples, the PL decay times are basically independent of the photoexcitation power. The excitation power dependence often allows one to distinguish between trapping and recombination centers: at carrier densities higher or similar to trap densities saturation of traps occurs, increasing the PL decay times. For the recombination centers, no such saturation is expected. For the 500 °C sample, judging from the ultrashort trapping time, the trap concentration may be too large to reach saturation even for the highest photoexcited carrier densities. For the other samples, the independence of the decay times on excitation power suggests that the defects, where carrier trapping occurs, are efficient recombination centers.

Recombination properties of implanted InP can be further explored on p-doped P⁺-implanted samples. The PL decay times obtained by a single-exponential fit for the samples annealed at 500 and 600 °C for high excitation powers (with respect to the concentration of equilibrium holes) are shown in Fig. 4. One can notice that for the samples annealed at 500 °C the PL decay times are much shorter. The same figure also shows PL decay times obtained for the sample annealed at 600 °C for low excitation conditions. In the p-doped implanted sample, the equilibrium holes are trapped to the implantation-induced defects, making them active electron traps. Thus, for low photoexcited carrier densities the PL intensity, which is proportional to the concentration of free electrons and holes, decays with the electron trapping time. For the high excitation power the PL decay time is longer. Assuming that in this case the electron traps are filled, the free electron and hole populations decay at the same rate, i.e., a new electron is trapped as soon as an electron trap is made active by trapping a hole. Then the PL decays with half the hole trapping time. The evaluated hole trapping times are around 6 ps and do not differ much from the electron trapping times, indicating that carrier dynamics in phosphorus ion-implanted InP is governed by recombination centers as well. This is advantageous for applications where device operation at high repetition frequencies is required.

Another interesting observation, which can be made from Fig. 4, is a relatively small dependence of the PL decay time (and the concentration of active traps) on the implantation dose. For the 600 °C annealing, the trapping times decrease by only about 25% when the ion dose is changed from $1 \times 10^{14}$ to $1 \times 10^{15}$ cm$^{-2}$, i.e., by an order of magnitude. The same tendency holds for the samples annealed at 500 °C. Such behavior may be understood by taking into account peculiarities of heavy ion implantation at elevated temperatures. Rutherford backscattering spectroscopy data show a broad plateau extending over several orders of magnitude in the damage dependence on the implanted ion density for the Si-implanted samples pointing to an equilibrium between defect production, recombination, and dynamic annealing. Similar data have been obtained for Fe⁺ implantation at 200 °C.

IV. DISCUSSION

A. Carrier traps in ion-implanted InP

At low doses, damage created by ion implantation into InP at elevated temperatures consists mainly of point defects and their complexes. The most common point defects are phosphorus and indium vacancies, interstitials, which often...
form pairs with vacancies, and antisite defects. In As-ion implanted GaAs, the main carrier traps are midgap As-antisite defects, similarly as in LT GaAs. In the analogous LT InP case, however, the P antisite is a shallow donor. For the P⁺-implanted InP, the samples turn n type and experience a decreased sheet resistance with increased implantation dose and annealing temperature (Fig. 2 and Ref. 7), and at high doses and annealing temperatures exhibit electrical properties similar to LT InP. Being smaller than indium, phosphorus can easily migrate at high annealing temperatures and occupy In vacancies produced during implantation, thereby creating P antisites and P vacancies. The P antisite is a known shallow donor while the P vacancies are deep donors. Thus, we suggest that in P⁺-implanted InP, the electrical properties are determined by phosphorus related defects, similarly as in LT InP.

For the Fe implanted samples, the situation is different; here the conductivity type changes from n to p, and the sheet resistance, lowest for the intermediate annealing temperatures, increases sharply for annealing temperatures above 800 °C. These results can be explained by a competition between shallow PIn-related donors and deep Fe-related acceptors. For the annealing at 600 and 700 °C, the shallow donors are already activated, but the Fe-related acceptors are not yet created at concentrations large enough to compensate the shallow donors. An increase in the annealing temperature causes Fe ions to diffuse and occupy In vacancy positions and/or form complexes with P vacancies, producing electrically deep acceptors. Consequently, the resistivity increases, and the equilibrium carrier concentration becomes very small as the annealing temperature is increased. The mobility in the as-implanted case is low, as expected for a material with a high concentration of defects. Upon annealing at 500 °C, $\mu_{\text{eff}}$ increases to $\sim 300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as the concentration of defects is reduced. The mobility then decreases with increasing annealing temperature as the degree of compensation of the material is increased.

While the change in electrical properties with implantation dose and annealing temperature demonstrates an interplay between the implantation-induced shallow donors and compensating acceptors, the PL dynamics is determined by deep carrier traps and recombination centers. Some insight into the origin of these defects can be obtained when plotting the PL decay rates as a function of the inverse annealing temperature in an Arrhenius-type plot for the Fe⁺-implanted samples (Fig. 5). As can be seen, all the points, except for the 900 °C sample, fall on a straight line producing an activation energy of $1.27 \pm 0.05 \text{ eV}$. This energy can be interpreted as energy needed to remove carrier traps by thermal annealing. The concentration of traps is proportional to the inverse PL decay time; with annealing temperature increased from 500 to 800 °C the trap concentration decreases over two orders of magnitude.

The obtained activation energy can be compared to 1.2 eV determined from the RBS and theoretical calculations for P vacancy migration and annihilation. Since phosphorus vacancies and their complexes, forming the deep traps, are produced during implantation in abundance, we consider them as plausible candidates for recombination centers determining the photoexcited carrier dynamics. These centers should be important for all Fe-implanted InP samples, except for the one annealed at 900 °C, for which a deviation from the Arrhenius dependence suggests a different origin of the main carrier traps. These are probably Fe related. Indeed, for $2 \times 14 \text{ cm}^2 \text{ Fe}^+$ dose implanted at 200 °C, the iron concentration within 1 μm from the surface is expected to be non-uniform based on TRIM simulations. The concentration of Fe is estimated to be in the range of $1 \times 10^{17} - 1 \times 10^{18} \text{ cm}^{-3}$. This matches fairly well to our $3 \times 10^{16} \text{ cm}^{-3}$ density of Fe⁺/Fe²⁺ centers, which would be responsible for the PL decay time of 46 ps, if trapping only to such centers were considered.

P vacancies and their complexes are produced during implantation independently of implantation species. Thus, vacancy-related recombination centers should be among the most important defects for carrier dynamics in any kind of implanted InP samples. To a certain degree, this is confirmed by similar trap activation energies for the Fe⁺- and P⁺-implanted samples (Fig. 5).

**B. Device considerations**

We find that both methods, implantation of p-InP with P⁺ and SI InP with Fe⁺ ions can be used to produce a material with subpicosecond response times, good mobility, and high resistivity. From the point of view of the shortest decay times, this is achieved in both cases for the lowest annealing temperature of 500 °C. The PL decay time resulting from Fe⁺ implantation into SI InP (130 fs) is shorter than that achieved with P⁺ implantation into p-InP (400 fs) and is due to the greater mass of Fe as compared to P, which translates into a greater amount of damage upon implantation. However, for device considerations, such a difference is not too important as 400 fs is a time short enough for most applications in ultrafast optoelectronics. P⁺ implantation into p-InP yields a material with a higher sheet resistance ($\sim 10^6 \Omega$/square) at 500 °C annealing, and both the sheet resistance and the decay time are weakly dependent on the implantation dose. This is highly desirable from a manufacturing point of view, where repeatability of results is of the utmost importance. P⁺ implantation of p-InP in this dose regime assures that good quality material for devices could be obtained with a large margin of error. In the Fe⁺ implantation case, the annealing temperatures needed to produce highly resistive
material result in decay times of the order of tens of picoseconds, disqualifying these materials for applications when both high resistivity and subpicosecond lifetimes are needed. Additionally, it appears that the dose dependence of the electrical characteristics of Fe$^+$-implanted InP is stronger.

V. CONCLUSIONS

We have analyzed two methods of achieving InP with ultrafast decay times, high sheet resistivities, and good mobilities: P$^+$ implantation into p-InP and Fe$^+$ implantation into semi-insulating InP at 200 °C. Both methods allow production of layers with high resistivity and good mobility. It was found that the carrier lifetimes can be tuned from ~100 fs to tens of picoseconds by implantation and annealing conditions. The dependencies of the electrical properties on the implantation dose and annealing temperature were explained by an interplay between shallow (for p-InP) or deep Fe-related (in the case of Fe$^+$ implanted) acceptors and phosphorus antisite-related shallow donors. Similar electron and hole trapping times observed in implanted samples indicate fast nonradiative carrier recombination, which is desirable in high-speed applications. The most advantageous implantation conditions for ultrafast device applications were found to be P$^+$ implantation into p-InP and annealing at 500 °C at any dose between $10^{14}$ and $10^{15}$ cm$^{-2}$. Such a treatment results in a material with a high resistivity, good mobility, and a short response time.