Variable temperature Hall-effect measurements in ion bombarded InP

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Abstract

Fe doped semi-insulating and p-type InP were implanted with P⁺ ions to produce an excess of phosphorous atoms in the order of 0.1 at.%. Subsequent annealing in Ar ambient in the temperature interval 400–600 °C was performed for 30 s in a rapid thermal annealing system. Variable temperature (12–300 K) Hall-effect measurements have been used for characteristic defect energy level extraction. A large amount of negative free carriers have been observed after the thermal treatments. These electrons are attributed to the creation of P_{In} antisite defects with an energy level above the minimum of the conduction band.

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PACS: 72.80.Ey; 61.72.Ji; 61.80.Jh
Keywords: Ion bombardment; InP; Mobility; Hall effect; Variable temperature

1. Introduction

Demand for increased speed in telecommunication systems has led to continued research into semiconductor materials for subpicosecond optoelectronic applications. The discovery of ultrafast carrier recombination characteristics in GaAs grown by molecular-beam epitaxy at low substrate temperatures (LT-GaAs) [1–3] created a new area of research in III–V technology – non-stoichiometric growth at low temperature. This is due to the fact that LT-GaAs has such superior characteristics as short carrier lifetime, high resistivity (∼10^5 Ωcm) and high-electron mobility. It has been shown recently that ion implantation of GaAs can result in a material with properties similar to those of LT-GaAs [4–6]. Broad studies made on LT-GaAs have led to the conclusion that non-stoichiometry of this material with a high-ar senic excess in the form of antisite defects and As precipitates is the main reason for high resistivity and fast recombination of photocarriers [7]. These results have stimulated efforts to understand electrical and structural properties of LT indium phosphide [8]. InP offers remarkable applications as a substrate in optical fiber communication systems, high frequency and high-power device applications, due to its outstanding electrical properties such as high-electron mobility and
high-breakdown field. It was found that the LT-InP epilayers were highly conductive and that the dominant intrinsic deep level defect was present in concentrations as high as \(10^{19}\) cm\(^{-3}\) [8]. The anti-site defects in III–V materials have been intensively studied, and particularly in GaAs, the arsenic anti-site is responsible for the semi-insulating behavior [9]. In InP, the presence of these defects has a different character, creating n-type free carriers [8]. The mechanism responsible for the n-type conductivity has been attributed to an abundant presence of PIn antisites with an energy level above the minimum of the conduction band, introduced during off-stoichiometric InP growth at low temperature, creating n-type free carriers. In the present paper we have investigated these defects using variable Hall-effect measurements in p-type and semi-insulating InP, implanted with P\(^+\) ions, creating an excess of phosphorous atoms in the material and allowing the formation of the mentioned PIn anti-site defects.

2. Experimental

Two sets of samples have been prepared for this investigation. A set of samples consisting of a p-type epilayer with concentration of \(1.3 \times 10^{18}\) cm\(^{-3}\) was grown to a thickness of \(\sim 1.5\) \(\mu\)m on semi-insulating InP (100) substrates by metal-organic chemical-vapor deposition and then implanted with P\(^+\) ions at energy of 1 MeV to doses between \(1 \times 10^{15}\) and \(1 \times 10^{16}\) cm\(^{-2}\). In a second set of semi-insulating Fe-doped InP samples, multiple implantation steps of P were performed in order to create a plateau-like concentration depth profile, extended from the surface to a depth of 0.6 \(\mu\)m. The doses and energies of the implantation steps (see Table 1) were determined by TRIM simulation [10]. All the implantations were carried out at 200 \(^\circ\)C with the sample surface normal tilted at 7\(^\circ\) with respect to the direction of incidence of the beam in order to minimize channeling effects. The implantation steps were performed sequentially from the highest to the lowest energy. Subsequently, the samples were annealed by rapid thermal annealing (RTA) at 400, 450, 500, 550 and 600 \(^\circ\)C for 30 s in an Ar atmosphere. Van der Pauw [11] structures have been prepared by manual deposition of point In contacts in the corners of square pieces and subsequent sintering at 200 \(^\circ\)C for 2 min in normal ambient. Variable temperature Hall-effect measurements have been used to determine defect energy levels and to understand carrier transport mechanisms.

3. Results and discussion

Fig. 1 shows the TRIM calculation of the additional phosphorous atom depth distributions in the p-type samples (Fig. 1(a)) and in the semi-insulating samples (Fig. 1(b)). In the p-type samples the P excess is \(\sim 1 \times 10^{19}\) cm\(^{-3}\) and in the SI-InP a plateau-like concentration depth profile, extended from the surface to a depth of 0.6 \(\mu\)m has

<table>
<thead>
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<th>Energy [keV]</th>
<th>400</th>
<th>130</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose [cm(^{-2})]</td>
<td>(2 \times 10^{15})</td>
<td>(1 \times 10^{15})</td>
<td>(3 \times 10^{14})</td>
</tr>
</tbody>
</table>

Table 1

P\(^+\) implantation parameters for the second set of samples (SI-InP)

Fig. 1. Phosphorous excess concentration in the (a) p-type InP and (b) semi-insulating InP samples, calculated by TRIM.
Table 2
Sheet carrier concentration ($p_s$), mobility ($\mu$) and sheet resistance ($R_s$) of phosphorous implanted p-type InP samples after 30 s RTA annealing at 500 °C in Ar ambient

<table>
<thead>
<tr>
<th>Dose [cm$^{-2}$]</th>
<th>$p_s$ [cm$^{-2}$]</th>
<th>$\mu$ [cm$^2$ V$^{-1}$ s$^{-1}$]</th>
<th>$R_s$ [Ω/sq]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \times 10^{14}$</td>
<td>$4.1 \times 10^9$</td>
<td>356</td>
<td>$4.2 \times 10^6$</td>
</tr>
<tr>
<td>$3.0 \times 10^{14}$</td>
<td>$2.7 \times 10^9$</td>
<td>430</td>
<td>$5.2 \times 10^6$</td>
</tr>
<tr>
<td>$5.0 \times 10^{14}$</td>
<td>$4.0 \times 10^9$</td>
<td>335</td>
<td>$4.6 \times 10^6$</td>
</tr>
<tr>
<td>$7.4 \times 10^{14}$</td>
<td>$6.4 \times 10^9$</td>
<td>331</td>
<td>$2.9 \times 10^6$</td>
</tr>
<tr>
<td>$1.0 \times 10^{15}$</td>
<td>$9.5 \times 10^9$</td>
<td>280</td>
<td>$2.3 \times 10^6$</td>
</tr>
</tbody>
</table>

been formed with P excess concentration in the interval of $4\text{–}8 \times 10^{19}$ cm$^{-3}$.

Dose dependence of the free carrier sheet concentration, mobility and sheet resistance in p-type samples, implanted with a P$^+$ and annealed in Ar ambient at 500 °C for 30 s and measured by Van der Pauw method, is shown in Table 2. One can see that all samples remain slightly p-type ($p_s \sim 3\text{–}9 \times 10^9$ cm$^{-2}$), effective mobility is relatively good ($\mu \sim 300\text{–}400$ cm$^2$ V$^{-1}$ s$^{-1}$), and the sheet resistance is in the order of MΩ/sq ($R_s \sim 2\text{–}5 \times 10^6$ Ω/sq). So, in the dose range studied, the implantation compensates the p-type material and a very high-sheet resistance was measured. Further experiments within this critical range could pinpoint the exact dose for transition from p- to n-type. This transition dose will also produce the highest-sheet resistance values for implanted p-type InP. Variable temperature Hall-effect measurements showed a characteristic deep level of the defect responsible for the compensation of $(0.31 \pm 0.02)$ eV above the valence band (not shown).

It has been found [12] that P$_{\text{In}}$ defect has two dominant donor levels: (0/+ and (+/+), with energy levels at 0.11 eV above and 0.23 eV below the minimum of the conduction band, respectively. The relatively low $R_s$ after n-type InP complete isolation by proton bombardment [13,14] is very likely due to the auto-ionization of the P$_{\text{In}}$ antisites, via excitation of (0/+ level. GaAs antisite defects are responsible for the semi-insulating behavior [15]. In InP the presence of these defects seems to have a different character – like traps or self-ionizing donor, depending on the energy level position [16]. Bombarding p-type material the holes are trapped in the single charged P$_{\text{In}}$ (+/+ defects) or are compensated with the electrons created via auto-ionization of P$_{\text{In}}$ (0/) antisites. For the n-type InP isolation the trapping in In$_p$ antisites competes with the free electron creation via auto-ionization of P$_{\text{In}}$ (0/) antisites [14].

The electrical changes to semi-insulating InP as a result of implantation with P and subsequent annealing at temperatures between 400 and 600 °C were investigated to prove the creation of those free carriers mentioned above. As it was published previously, annealing at high temperatures (600 °C) is required to remove strain and reduce defects introduced during implantation [17]. This also results in a material with high mobility, high-sheet carrier concentration and low resistivity.

Fig. 2 shows the Hall-effect results for P$^+$ multiple implantations at 200 °C (see Table 1) into SI-InP samples, subsequently annealed at temperatures 400, 450, 500, 550 and 600 °C. It can be seen (Fig. 2(a)) that the mobility is continuously increasing above 450 °C, due to electrically active complex defect dissolution and annihilation. The free carrier sheet concentration (Fig. 2(b)) reaches saturation at 500–550 °C, which corresponds to the decrease in the sheet resistance (Fig. 2(c)).

We examine the possibility for creation of these free carriers, due to a disruption of the Fe doping sites, whose role in the substrate is to compensate for inevitable shallow donor formation during crystal growth, allowing the donors to reactivate and contribute to the large-sheet carrier concentration. The typical Fe doping concentration is $1 \times 10^{16}$ cm$^{-3}$, resulting in a sheet concentration of $6 \times 10^{11}$ cm$^{-2}$ in a 0.6 μm-thick implanted layer of InP. Thus, even if all the Fe acceptors were deactivated, the maximum increase in $n_s$ that could be achieved by this mechanism is of the order of $6 \times 10^{13}$ cm$^{-2}$. It can be seen that at annealing temperatures greater than 500 °C, $n_s$ is in excess of $10^{13}$ cm$^{-2}$. Hence, one can conclude that these shallow donor-like levels are created by defects and phosphorous excess in the crystal structure itself, as a result of the implantation and annealing process [18].

Fig. 3 shows the variable temperature Hall-effect measurements for the samples shown in Fig. 2, annealed at temperatures 500, 550 and 600 °C. The relatively low $R_s$ (100 Ω/sq for annealing at 600 °C) is very likely due to the auto-ionization of the P$_{\text{In}}$
antisites [13,14], via excitation of (0/+) level. In InP the presence of these defects seems to have the character of self-ionizing donor. One can note the uncommon mobility temperature dependence. The effective mobility (Fig. 3(a)) is continuously increasing for the 500 °C annealed sample. This is due to a very large Coulomb scattering center concentration, mentioned above, which dislocate the mobility maximum temperature for a value >300 K. Fig. 4 shows the electron sheet concentration of the same sample, as a function of temperature. The fit (dashed line) yields the activation energy of the level responsible for the variation of the sheet carrier concentration at 300 K. The extracted value is $E_A = 0.38 - 0.42$ eV, indicating that the Fermi level is pinned within the bandgap.

4. Conclusions

We have investigated the creation of special shallow donor-like levels during ion bombardment and subsequent annealing of InP. Free electrons are created via auto-ionization of P_{In} (0/+) antisites.

The results thus far have indicated that it is possible to create a good quality material with a good mobility by implanting semi-insulating InP
and annealing at high temperatures, but at the expense of low-sheet resistance. Low-sheet resistance is associated with high-dark currents in photodetectors and is therefore considered undesirable. However, such materials may still find application as saturable absorbers for the mode locking of solid-state lasers.

By choosing the appropriate implant dose, p-type hole concentration, and annealing temperature, p-type InP implanted with P ions could be used for the fabrication of ultrafast photodetectors. For p-type InP with a hole concentration of $1.3 \times 10^{18}$ cm$^{-3}$, the critical dose is in the range of $1 \times 10^{14} - 1 \times 10^{15}$ cm$^{-2}$.

Acknowledgements

This work was partly supported by Brazilian Agencies FAPERGS, CAPES and CNPq.

References


Fig. 4. Electron sheet concentration as a function of temperature of the semi-insulating InP sample multiple implanted with P$^+$, annealed at 500 °C for 30 s in Ar ambient.