RAMAN AND ELECTRICAL CHARACTERIZATION OF n-InP IMPLANTED BY 630-keV NITROGEN

I. M. Tiginyanu^{1,3}, J. Miao¹, H. L. Hartnagel¹, D. Rück², K. Tinschert², V. V. Ursaki³, V. M. Ichizli³

¹ Institut für Hochfrequenztechnik, Technische Hochschule Darmstadt, Merckstr. 25, D-64283 Darmstadt - Germany

Phone: +49.6151.165372, Fax: +49.6151.164367, e-mail: hfmwe101@hrzpub.th-darmstadt.de

² GSI, Postfach 11 05 52, D-64220 Darmstadt - Germany

³ Institute of Applied Physics, 277028 Kishinev - Moldova

Introduction

Over the last years, increasing attention has been paid to the problem of ion-beam induced isolation of InP-based materials (1, 2). Strong conductivity compensation was reached, for example, by Ti⁺-implantation in p-InP (3) and Fe⁺-implantation in n-InP (4). However, implantation of heavy ions like Ti⁺ and Fe⁺ considerably damages the samples resulting in poor lattice quality even after high-temperature annealing. This problem becomes more severe in case of ion-induced amorphization since indium phosphide, like other III-V materials, shows very poor recrystallization characteristics (1). Due to these reasons, implantation of light ions proves to be more attractive for generating thick high-resistance layers. The goal of this work was to study the peculiarities of lattice disorder and conductivity compensation caused by 630-keV N*-implantation in liquid encapsulated Czochralski grown n-InP single crystals. The ion-induced damage of the lattice was probed by resonant Raman scattering (RS) measurements. Layers with resistivity as high as 10⁴ Ω·cm were formed by implantation and subsequent annealing of the samples which allowed one to fabricate InP membranes for sensor applications by using selective electrochemical etching techniques.

I. Experimental

(100)-oriented n-InP samples (n = 2×10^{17} cm³ at 300 K) were implanted by N⁴-ions using a dose of 5×10^{14} cm². The implantation was carried out at room temperature, the wafers being tilted to minimize channelling. According to TRIM (transport of ions in matter) simulations (5), in this case the projected ion range peak R_p is centered at a depth of 0.95 µm. After implantation, the samples were passivated with a 200-nm thick plasma enhanced chemical vapour deposition (PECVD) layer of Si_3N_4 and annealed in an atmosphere of flowing hydrogen for 10 min at different temperatures between 400 and 750°C. To

measure the resistivity of the implanted layers, the back side of samples was completely covered by an ohmic contact and 200-µm diameter dot contacts were formed on the front side. Ni-AuGe-Ni evaporation with subsequent rapid thermal annealing of samples were used for fabrication of these ohmic contacts.

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 spectrometer with the spectral resolution 2 cm⁻¹ or less. The excitation of Raman spectra was provided by the 514.5-nm line (200 mW) of an argon laser. At this

wavelength the penetration depth of the light in the implanted layers was about 100 nm. The depth distribution of ion-induced defects was evaluated by RS measurements combined with etch-removal of layers. Standart photon counting techniques were used.

II. Results

A. Raman Spectra

RS spectra of N*-implanted n-InP are presented in Fig. 1. The undamaged regions of the sample (curve 4) exhibit only the LO-phonon RS at 348 cm⁻¹, in accordance with the selection rules of crystals with the zinc-blende structure. N⁺implantation leads to more complex Raman spectra where the LO-phonon peak is shifted to lower frequencies and broadened. The RS band at 308 cm⁻¹ corresponds to the TO-phonon which is forbidden in the configuration involved. The appearance of this band in the (100)-geometry can be attributed to the breakdown of the selection rules caused by the disorderinduced destruction of the quasimomentum conservation. The peak at about 270 cm⁻¹ represents a second-order one (6) which is also induced by ion implantation.

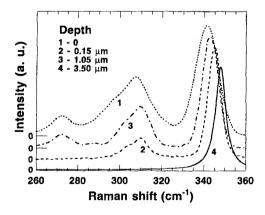


Fig. 1. Normalized Raman spectra of N⁺-implanted n-InP, taken on the original surface of the sample and after etch-removal of layers.

Since the position of the LO-phonon band in RS spectra is most sensitive to the lattice disorder (7), it can be used in order to get information about the damage-depth profile in ion-implanted materials (8). Analysis of data presented in Fig. 1 allowed one to reveal a pronounced disorder in the near surface region of N*-implanted n-InP probably related to stoichiometric disturbances caused by nonequal recoil of In and P atoms (9). As to the maximum of the damage-depth-profile, it occurs at about $0.8R_p$, which is in good agreement with earlier observations (1).

In order to study the process of the crystal lattice recovery, measurements of RS spectra were performed on InP samples subjected to post-implantation annealing. A partial annealing of defects was evidenced when annealing temperatures were lower than 600°C. In Fig. 2 we show the effect of sample annealing at 450 °C on the Raman of N⁺-implanted n-InP. This spectrum spectrum differs from both curves 1 and 4 illustrated in Fig. 1 which is indicative of a partial recovery of the lattice. At the same time the RS spectrum after the sample annealing at 600°C practically coincided with the one of the as-grown crystals. It is to be noted that similar effect was observed recently in He⁺-implanted n-InP (10).

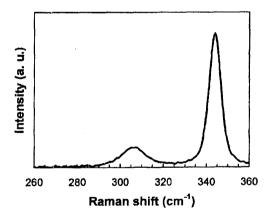


Fig. 2. RS spectrum of N*-implanted n-InP after annealing at 450 °C.

B. Conductivity Compensation

Fig. 3 shows the resistivity of N-implanted n-InP layers subjected to annealing at different temperatures. A weak dependence of resistivity upon annealing temperature was evidenced in

the interval 400 to 600°C. After reaching the maximum value of about 10^4 Ω ·cm at 600°C, the resistivity diminishes with further increase of T_{ann} .

It has been established earlier (1, 11) that radiation treatment of InP leads to the Fermi-level pinning in the upper half of the band gap. This effect was explained by the predominance in the crystal lattice of a donor-like defect having 0.4-eV ionization energy (12). Due to this fact the resistivity of n-InP can be increased only to the 10³-10⁴ Ω·cm range as it is seen in Fig. 3. In the case of N⁺-implanted n-InP the layers with increased resistivity are stable up to the annealing temperatures of about 600°C. For the purpose of comparison one can note, that after high-energy B⁺-implantation in n-InP the layer resistivity exhibits a sharp diminution with increasing T_{ann} beginning from annealing temperatures of 400-500°C (13). The conductivity compensation in N^{+} implanted n-InP crystals allowed one to fabricate InP membranes, as described below.

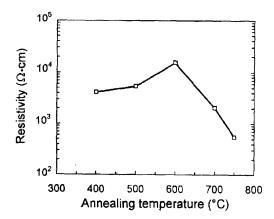


Fig. 3. Resistivity of N^* -implanted n-InP layers versus annealing temperature.

C. Membrane Fabrication

N*-implanted n-InP annealed at 450 °C has been used for the purpose of fabricating a membrane. A 200-nm thick SiO₂ layer was deposited on the front side of samples. After that the membranes pattern was defined by photolithography and wet chemical etching in a solution based on CH₃COOH, HCl and H₂O₂. This non-selective etching produced in

InP samples 2- μm depth holes with almost vertical side walls.

Subsequently, the InP samples were subjected to a pulsed anodic selective etching using 10-V pulses with a duration of 100 µs, this electrochemical process having been carried out in a simple two-electrodes cell as described earlier (14, 15). A Pt-bath based on H₂PtCl₆, H₃PO₄ and H₂SO₄ was used as electrolyte. The high-resistance N⁺implanted surface layer proved to be not etched by the process involved, leaving an approx. 1-um thick membrane. Fig. 4 illustrates a scanning electron microscope (SEM) micrograph of a high-resistance InP membrane covered by 200-nm thick SiO, film. One can see that a part of unimplanted indium phosphide removed by the selective electrochemical etching leading to the formation of a welldefined cavity below the membrane.



Fig. 4. SEM-micrograph of a high-resistance InP membrane.

III. Conclusion

Raman scattering was shown to be an useful tool for studying the lattice disorder versus depth in ion-implanted InP. A conductivity compensation was reached in n-InP by N*-implantation and subsequent annealing in the temperature interval from 400 to 600°C. Although the values of resistivity are moderate (up to 10⁴ Ω ·cm), they prove to be sufficient for the purpose of fabricating InP membranes by using selective anodic etching techniques. This important feature opens new possibilities for applications of InP.

Acknowledgements

I.M.T. gratefully acknowledges the supports of the Alexander von Humboldt Foundation and of the Technische Hochschule Darmstadt. J.M. thanks the Gesellschaft für Schwerionen-forschung (GSI) for the financial support.

References

- (1) S.J. Pearton, Int. J. Modern. Physics, Vol. B7, pp. 4687-4761, 1993.
- (2) M.C. Ridgway, R.G. Elliman, M.E. Faith, P.C. Kemeny, M. Davies, Nucl. Instr. Meth. in Phys. Res., Vol. B96, pp. 323-326, 1995.
- (3) J.M. Martin, R.K. Nadella, J. Vellanki, M.V. Rao, O.W. Holland, J. Appl. Phys., Vol. 73, pp. 7238-7243, June 1993.
- (4) A. Carnera, A. Gasparotto, M. Tromby, M. Caldironi, S. Pellegrino, F. Vidimari, J. Appl. Phys., Vol. 76, pp. 5085-5094, November 1994.
- (5) J.P. Biersack, L.G. Haggmark, Nucl. Instrum. Methods, Vol. 174, pp. 257-269, 1980
- (6) S.J. Yu, H. Asahi, Sh. Emura, H. Sumida, Sh. Gonda, H. Tanoue, J. Appl. Phys., Vol. 66, pp. 856-860, July 1989.

- (7) K.K. Tiong, P.M. Amirtharaj, F.H. Pollak, Appl. Phys. Lett., Vol. 44, pp. 122-124, January 1984.
- (8) G. Braunstein, D. Tuschel, S. Chen, S.-T. Lee, J. Appl. Phys., Vol. 66, pp. 3515-3522, October 1989.
- (9) L.A. Christel, J.F. Gibbons, J. Appl. Phys., Vol. 52, pp. 5050-5055, August 1981.
- (10) I.M. Tiginyanu, A.I. Terletsky, V.V. Ursaki, Solid State Commun., Vol. 96, pp. 789-792, October 1995.
- (11) N.B. Pyshnaya, S.I. Radautsan, I.M. Tiginyanu, V.V. Ursaki, V.A. Ursu, I.M. Aliev, H.A. Halilov, Cryst. Res. Technol., Vol. 26, pp. K129-K135, 1991.
- (12) N.B. Pyshnaya, I.M. Tiginyanu, V.V. Ursaki, Semiconductors, Vol. 28, pp. 1-3, January 1994.
- (13) R.K. Nadella, J. Vellanki, M.V. Rao, O.W. Holland, J. Appl. Phys., Vol. 72, pp. 2179-2184, September 1992.
- (14) A. Grüb, K. Fricke, H.L. Hartnagel, J. Electrochem. Soc., Vol. 138, pp. 856-857, 1991.
- (15) J. Miao, H.L. Hartnagel, B.L. Weiss, R.J. Wilson, Electron. Lett., Vol. 31, pp. 1047-1049, June 1995.