Vol. 82 (1992) *ACTA PHYSICA POLONICA A* No 5

Proceedings of the XXI International School of Semiconducting Compounds, Jaszowiec 1992

DEFECTS STUDIES IN AS GROWN AND NEUTRON IRRADIATED PHOSPHORUS RICH GaP*

J. JASIŃSKI[a], M. PALCZEWSKA[b], K. KORONA[a], M. KAMIŃSKA[a], E.D. BOURRET[c] AND G. ELLIOT[d]

[a]Institute of Experimental Physics, Warsaw University
Hoża 69, 00-681 Warszawa, Poland
[b]Institute of Electronic Materials Technology
Wólczyńska 133, 01-919 Warszawa, Poland
[c]Lawrence Berkeley Laboratory, Berkeley, CA 94720 USA
[d]Hewlett Packard, San Jose, CA 95131 USA

Semi-insulating, *p*- and *n*-type liquid encapsulated Czochralski grown phosphorus rich GaP crystals before and after neutron irradiation were studied. EPR measurements proved that the phosphorus antisite defect P_{Ga} introduced by neutron irradiation was exactly the same as in as grown materials, i.e. surrounded by four substitutional phosphorus atoms. In neutron irradiated crystals EPR showed also a signal, similar to the one found in plastically deformed GaAs and GaP. The concentrations of P_{Ga} and of the other defect were estimated to be of the same order of magnitude. Two absorption bands at 0.81 and 1.12 eV were found for irradiated materials. The temperature dependence of resistivity indicated hopping as the mechanism of conduction in samples irradiated with doses higher than $\approx 4\times10^{16}$ cm^{-2}.

PACS numbers: 71.55.Eq, 78.50.Ge, 76.30.Mi

Antisite defects have been found to be dominant native defects in III–V semiconductors. However, there is no common agreement on their exact microscopic structure, particularly it is not clear if antisite defects in as grown crystals are the same as introduced by irradiation or plastic deformation.

In this paper antisite defects in liquid encapsulated Czochralski (LEC) grown phosphorus rich GaP crystals were studied. Semi-insulating (SI), *p*- and *n*-type materials of concentration 1.5×10^{16} and 3×10^{15} cm^{-3} respectively were used. The samples cut from these crystals were irradiated by fast neutrons with doses of 3.8×10^{15}, 4.1×10^{16}, 3.7×10^{17}, 3.0×10^{18}, $\approx 8\times10^{18}$ cm^{-2} in the core MARIA at Świerk.

In spite of expected domination by phosphorus antisite signal, EPR spectra of neutron irradiated materials at 4.2 K revealed broad, well-resolved new structure WA1, with $g\approx 2.1$. The angular dependence of that signal was investigated

*This work is supported in part by the Committee for Scientific Research 2 0179 91 01 grant.

(Fig. 1). The lower field part did not change with the direction of magnetic field but a strong dependence appeared at the higher field part of the spectrum. For the magnetic field parallel to [100] direction only four lines were resolved. But when the

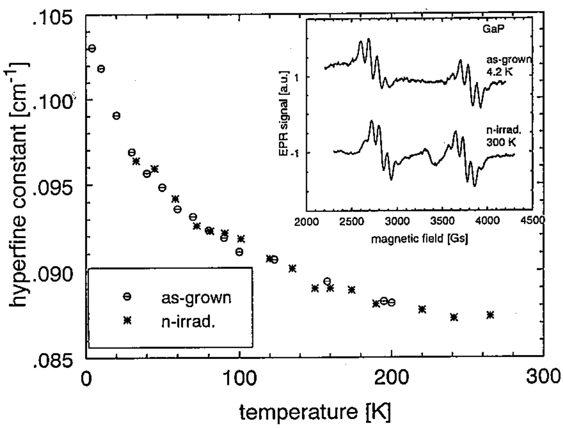

Fig. 1. Temperature dependence of hyperfine interaction constant of $P_{Ga}P_4$ for as grown and neutron irradiated crystals.

field was parallel to [111] and especially to [110] direction the fifth line appeared. The EPR signal similar to WA1 has been observed for electron irradiated GaAs [1, 2] and for plastically deformed GaAs [2–4] and GaP [5, 4]. The WA1 signal decreased rapidly with the increase in temperature and almost disappeared at 60 K. With the decrease in WA1 signal the spectrum consisting of two groups of five lines (P_{Ga}-like signal) started to be detected. The temperature dependence of hyperfine constant of this spectrum (approximately the difference between resonant fields at which two groups are measured) was identical to that for $P_{Ga}P_4$ EPR signal observed in SI GaP (Fig. 2). In addition, the angular behaviour of the spectrum which appeared in neutron irradiated materials was exactly the same as that investigated for $P_{Ga}P_4$ cluster in SI GaP [6]. These experimental results indicated that *the isolated phosphorus antisite surrounded by four substitutional phosphorus atoms was created by neutron irradiation of GaP crystals.* The $P_{Ga}P_4$ spectrum in neutron irradiated materials revealed unusual temperature behaviour. The signal increased almost linearly with temperature up to 200 K where the saturation took place. Up to now the explanation of this effect is unknown.

Relative changes with dose of both intensities of the $P_{Ga}P_4$ signal measured at 300 K and that of WA1 measured at 4.2 K were very similar. At low doses these intensities were scaling linearly with fluency and started to saturate with increase in dose. Finally at $\approx 8 \times 10^{18}$ cm^{-2} they were almost completely saturated. Intensity of the $P_{Ga}P_4$ signal measured at 300 K was nearly two order of magnitude less than that of WA1 measured at 4.2 K. But assuming variation of EPR signal proportional to reciprocal temperature one can estimate that concentrations of the two observed defects were comparable, irrespective of neutron dose. This

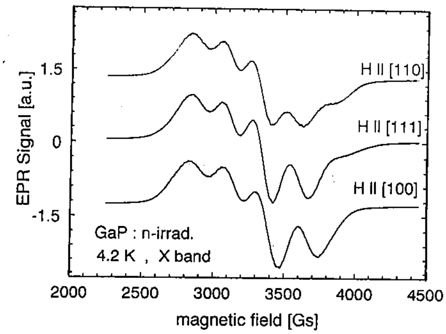

Fig. 2. The angular dependence of the WA1 signal for neutron irradiated GaP crystals.

concentration was estimated to be a few of 10^{17} cm^{-3} for dose $\approx 8 \times 10^{18}$ cm^{-2}.

Infrared absorption measurements were done for samples irradiated with doses of 3.8×10^{15}, 4.1×10^{16} and 3.7×10^{17} cm^{-2}. Samples irradiated with higher doses were not transparent. A typical absorption spectrum obtained for these materials consisted of two bands at 0.81 and 1.12 eV situated at large background (Fig. 3). Any fine structures related with these bands were not observed. Both of the bands changed nearly linearly with dose and were almost proportional one to the other. The origin of the two bands is most probably one of the two defects observed by EPR. Annealing experiments may solve this problem.

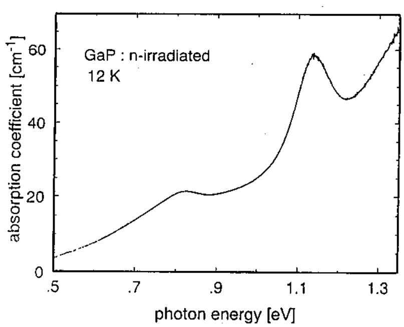

Fig. 3. An IR absorption spectrum obtained for GaP crystal after neutron irradiation with the dose of 3.7×10^{17} cm^{-2}.

The transport measurements showed that at lowest dose of irradiation the resistivity of the crystals increased and its value was about 10^{12} Ω cm at 300 K, whereas the resistivities of as grown materials were equal to $\approx 10^{13}$, $\approx 10^{2}$ and $\approx 10^{3}$ Ω cm for SI, *p*- and *n*-type respectively. At higher doses the resistivity decreased with dose and for crystals irradiated with $\approx 8 \times 10^{18}$ cm^{-2} it was equal to $\approx 10^{5}$ Ω cm. The explanation of such behaviour of resistivity is the following. The irradiation of crystal by neutrons of the dose 3.8×10^{15} cm^{-2} introduced enough number of defects which took part in compensation and caused material to be semi-insulating. At higher doses the concentration of defects was large and a new type of conduction appeared at lower temperature — it was hopping between defect centers. The temperature dependence of resistivity seemed to confirm that interpretation. Indeed, at higher doses the additional conduction existed. It increased with increase in dose. The temperature dependence of it was proportional to $\exp((T_0/T)^{1/4})$ at lower and to $\exp(-E_3/kT)$ at higher range of temperature. Such a behaviour has been predicted by the theory of hopping conduction on shallow impurities and it was observed in hopping between deep defects in neutron irradiated GaAs [7] and low-temperature (LT) GaAs.

In summary, neutron irradiation of GaP was found to introduce phosphorus antisite defect of exactly the same microscopic nature as antisite defect in as grown GaP. For high irradiation doses the hopping conduction between the centers was observed.

References

[1] A. Goltzene, B. Meyer, C. Schwab, *J. Appl. Phys.* **57**, 5196 (1985).

[2] E. Christoffel, A. Goltzene, C. Schwab, W. Guangyu, W. Ju, paper presented at *5th Conf. Semi-Insulating III-V Mater., Malmö (Sweden)*, 1988.

[3] M. Wattenbach, J. Krüger, C. Kisielowski-Kemmerich, H. Alexander, *Mater. Sci. Forum* **38-41**, 73 (1989).

[4] J. Palm, C. Kisielowski-Kemmerich, H. Alexander, *Appl. Phys. Lett.* **58**, 68 (1991).

[5] J. Krüger, H. Alexander, *Mater. Sci. Forum* **83-87**, 988 (1992).

[6] U. Kaufmann, J. Schneider, R. Wörner, T.A. Kennedy, N.D. Wilsey, *J. Phys. C, Solid State Phys.* **14**, L951 (1981).

[7] R. Coates, E.W.J. Mitchell, *J. Phys. C, Solid State Phys.* **5**, L113 (1972).