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

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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 $4 \times 10^{16}$ cm$^{-2}$.

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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 $1.5 \times 10^{16}$ and $3 \times 10^{15}$ cm$^{-3}$ respectively were used. The samples cut from these crystals were irradiated by fast neutrons with doses of $3.8 \times 10^{15}$, $4.1 \times 10^{16}$, $3.7 \times 10^{17}$, $3.0 \times 10^{18}$, $\approx 8 \times 10^{18}$ 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

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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 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 (PGaP₄-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 PGaP₄ 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 PGaP₄ 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 PGaP₄ 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 PGaP₄ 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 ≈ 8 x 10¹⁸ cm⁻² they were almost completely saturated. Intensity of the PGaP₄ 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
concentration was estimated to be a few of $10^{17} \text{ cm}^{-3}$ for dose $\approx 8 \times 10^{18} \text{ cm}^{-2}$.

Infrared absorption measurements were done for samples irradiated with doses of $3.8 \times 10^{15}$, $4.1 \times 10^{16}$ and $3.7 \times 10^{17} \text{ cm}^{-2}$. 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.

The transport measurements showed that at lowest dose of irradiation the resistivity of the crystals increased and its value was about $10^{12} \Omega \text{ cm}$ at 300 K, whereas the resistivities of as grown materials were equal to $\approx 10^{13}$, $\approx 10^2$ and $\approx 10^3 \Omega \text{ cm}$ for SI, $p$- and $n$-type respectively. At higher doses the resistivity decreased with dose and for crystals irradiated with $\approx 8 \times 10^{18} \text{ cm}^{-2}$ it was equal to $\approx 10^5 \Omega \text{ cm}$. The explanation of such behaviour of resistivity is the following. The irradiation of crystal by neutrons of the dose $3.8 \times 10^{15} \text{ cm}^{-2}$ 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 \( \exp((-E_3/kT)) \) at lower and to \( \exp((T_0/T)^{1/4}) \) 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 phosphorous 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