THE LUMINESCENCE AND EPR CHARACTERSATION OF NEUTRON TRANSMUTATION DOPED GALLIUM PHOSPHIDE*

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The photoluminescence and EPR measurements of neutron irradiated and annealed GaP samples are presented. Both methods confirm the presence of neutral GeGa. The EPR spectrum gives also an indication of interstitial Ge.

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Nuclear Transmutation Doping (NTD) enables doping of semiconductor crystals, independent of their growth conditions [1]. In this method the dopant is generated in the crystal volume as a result of thermal neutron irradiation. Owing to the low capture cross-section of thermal neutrons by host lattice atoms, the distribution of transmutation-induced dopants is homogeneous and nearly independent of the diameter and size of the semiconductor crystals.

In this paper we present the results of photoluminescence (PL) and EPR measurements on thermal neutron irradiated and annealed GaP. When GaP is irradiated with thermal neutrons, both of its elements are transmuted and the isotopes $^{70}$Ge and $^{32}$S are formed [2]. The cross-section ($\sigma_{th}$) for the formation of the Ge isotopes is much larger than for the S isotope creation. Therefore, during the neutron irradiation process, mainly Ge dopants are generated. The transmuted Ge and S nuclei experience the recoil due to the subsequent $\beta$ and $\gamma$ emissions. Thus, the position of Ge or S atoms in the unit cell is not necessarily a substitutional...

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Simultaneously with the transmutation process, various types of defects are inevitably generated during neutron irradiation of GaP crystals. The radiation damage can be almost entirely removed by an appropriate annealing.

The samples used in this experiment were (110) LEC GaP doped with sulphur. The neutral donor concentration, determined as in [3], was found to be $7 \times 10^{17} \text{cm}^{-3}$. The neutron irradiation of the samples was performed at the EWA reactor facility of the Institute of Atomic Energy in Warsaw. The ratio of thermal to fast neutrons was 1000 : 1. The thermal neutron flux was $1.4 \times 10^{19} \text{cm}^{-2}$. Such dose leads to the formation of $1.1 \times 10^{18} \text{cm}^{-3}$ of Ge atoms and $7 \times 10^{16} \text{cm}^{-3}$ of additional S atoms. The sample annealing was performed in vacuum at 800° C. The photoluminescence measurements were made at 2 K using a germanium detector and an Ar+ laser as an excitation source. The PL spectra are shown in Fig. 1. The EPR measurements were made with a Bruker B–ER 418 S spectrometer (at $X$ band, $f = 9.248 \text{GHz}$) and at 10 K. The EPR spectrum is shown in Fig. 2.

![Fig. 1. The luminescence of the annealed S doped GaP (a), of the NTD GaP (b), and of GaP intentionally doped with Ge (c).](image)

The Hall measurements on neutron irradiated sample [4] show that the sample is $n$-type, with the Fermi level at 200 meV below the conduction band. This value coincides with the ionisation energy of Ge$_\text{Ga}$ donors (equal to 204.5 meV according to [5]).

The single PL band in the NTD GaP (shown in Fig. 1) consists of two overlapping emissions which were not observed before the NTD process. These emissions replace the $S_p$ related transitions and thus we attribute them to Ge$_\text{Ga}$. One of
them is the donor-acceptor pair (DAP) recombination involving the Ge donor and an unidentified deep acceptor [6]. This is also confirmed by an independent ODMR experiment [7]. The structured PL spectrum of the melt-doped GaP:Ge is due to various complexes and uncontrollable contaminants. The homogeneity of the NTD material, as checked by excitation-spot PL dependence, is far better than for the starting material or GaP intentionally doped with Ge.

The observed EPR spectrum (Fig. 2) is composed of a broad isotropic line with the $g$-factor of 2.00. The EPR feature can be attributed to GeGa, in agreement with the previous observation [8]. The broad spectrum ($\Delta H_{pp}$ of 20.4 mT) overlaps with another structured one which has the similar $g$-factor. The observed structure is due to the P ligand hyperfine splitting (average line distance of 13 mT). The fact that the EPR spectrum consists of two components was confirmed by an independent K band experiment and photo-EPR data. The angular dependence of the EPR spectrum indicates that the defect responsible for the structured spectrum has a cubic symmetry, isotopic spin zero and four P neighbors. This is also a state with a localized wave function, otherwise the structure would not be seen. The observed ligand hyperfine splitting is inconsistent with the one determined from ENDOR for substitutional S and Ge donors [9, 10], but a Ge interstitial is a plausible candidate to account for this EPR signal.

In conclusion, we demonstrate the feasibility of NTD of GaP and the advantages of this method over the melt-doping. Our luminescence data show that the Ge donor and only one dominant acceptor play a role in radiative recombination and the neutral GeGa is the main paramagnetic center present in the NTD GaP.
crystals.

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