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Neutron transmutation doping of GaP: optical studies

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An unambiguous proof for successful neutron transmutation doping (NTD) of GaP is presented on the basis of optically detected magnetic resonance (ODMR). GaP:S samples grown by the liquid encapsulated Czochralski method were irradiated with thermal neutrons and subsequently annealed at 800 °C. In the ODMR experiments the transmuted Ge substitutional on Ga sites was detected. The NTD process was also found to create deep acceptors, the nature of which will be tentatively discussed.

1. Introduction

In this communication we present results of photoluminescence (PL) and optically detected magnetic resonance (ODMR) studies on GaP irradiated with thermal neutrons and subsequently annealed. Thermal neutron capture transmutes both constituent elements of GaP, Ga to Ge and P to S. The cross-section for neutron capture by Ga is about 40 times larger [1]. Hence, neutron irradiated GaP is expected to be essentially doped with Ge. Neutron transmutation doping (NTD) is a well-established method for n-type doping of Si. The quality of high-power electronic devices was highly improved due to doping homogeneity and low defect concentration of the NTD Si. Much less attention was paid to transmutation doping of III–V compounds. Till very recently no definite proof existed for successful NTD of GaP.

As the starting material we used commercially available n-type GaP:S grown by the liquid encapsulated Czochralski (LEC) method. The doping level prior to irradiation was 7×10^{17} cm^{-3}. Neutron irradiation was performed at SWIERK Nuclear Research Centre in Poland with the ratio of thermal to fast neutrons being 1000 : 1. The thermal neutron fluence was 1.4×10^{19} cm^{-2} yielding 1.1×10^{18} Ge atoms/cm^3 and 7×10^{16} S atoms/cm^3. After irradiation most of the Ge and S dopants are in interstitial positions. Subsequent sample annealing is necessary to render them substitutional. We used the annealing procedure of Huber et al. [1] (800 °C for 1 h) who first tried to dope GaP by NTD. However, they applied a rather small neutron fluence and could only indirectly conclude on NTD of GaP. After neutron irradiation and 800 °C 1 h annealing Hall effect measurements [2] showed n-type sample conductivity with the thermal activation energy of 200 ± 10 meV. This agrees well with the value of 204 meV reported for GaP conventionally doped with Ge and is thus indicative of successful NTD. Here we will show directly by PL and ODMR that after irradiation and annealing the transmuted Ge enters the Ga site forming Ge_{Ga} donor states. Secondly, the observation of Huber et al. [1] that NTD introduces also some acceptor states which are not annealed out even at 800 °C will be confirmed. The nature of these deep Ge related acceptors will be discussed.

2. Experiment

PL measurements were performed at 4.2 K using CW Ar^{+}-laser excitation (514.5 nm).

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Luminescence was dispersed by a 1.5 m high-resolution monochromator and detected with a Ge detector using standard lock-in techniques. The ODMR experiments were carried out at 2.1 K at 35 GHz, using a split-coil superconducting magnet in the Faraday configuration. Samples were mounted in a cylindrical TE_{011} cavity with slits for optical access. Changes of total emission intensity were monitored in phase with on–off modulated microwaves with the monochromator set to zeroth order. The spectral dependence of the ODMR signals was investigated by setting the magnetic field to resonance and scanning through the luminescence. More experimental details may be found elsewhere [3].

Four different samples, labelled (a) to (d), were used in the experiments: (a) the starting material LEC GaP:S, (b) the starting material annealed in vacuum for 1 h at 800 °C, (c) the as-irradiated sample and (d) the NTD sample which was irradiated and subsequently annealed for 1 h at 800 °C.

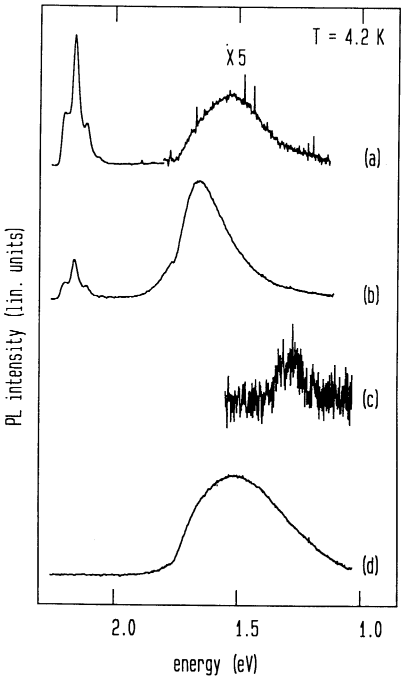

Fig. 1. PL spectra measured at 4.2 K of (a) the starting material LEC GaP:S (b) annealed (800 °C, 1 h), (c) as-irradiated and (d) irradiated and subsequently annealed (800 °C, 1 h). Spectra are measured under 514.5 nm Ar^+ excitation with a 1.5 m monochromator and a Ge detector.

3. Results and discussion

The PL spectra – see fig. 1 – of samples (a) and (b) differ slightly in their ratios of edge and deep emission as well as in their relative intensities of the 1.5 and 1.7 eV PL bands. The as-irradiated material (c) was non-transparent due to a high concentration of radiation defects caused by β and γ recoil during transmutation. Hence, only a very weak emission could be observed peaking at 1.25 eV. After annealing – sample (d) – this band appears as a low energy shoulder on the dominating 1.52 eV PL band. The ODMR spectra – see fig. 2 – of samples (a) and (b) show the characteristic S donor resonance signal with an isotropic value of $g = 1.99 \pm 0.01$. At slightly lower field an overlapping acceptor-related signal is observed. These ODMR signals are observed on the 1.5–1.6 eV luminescence – see fig. 3b – in agreement with previous observations [5]. Due to the very weak PL of sample (c) no ODMR spectrum could be observed. The resonance spectrum of the NTD GaP sample (d) shows a single isotropic resonance line (53 mT broad) with $g = 2.00 \pm 0.01$. The identical spectrum was previously observed for conventionally doped LEC GaP:Ge, both in EPR [4] and ODMR [5]. Consequently, we identify this signal with the substitutional Ge donor centre. This donor signal is an enhancement of the 1.25 eV emission – see fig. 3d – proving the donor-acceptor pair (DAP) nature of this emission. The 1.52 eV PL dominant for the NTD sample shows only a very weak ODMR signal identical to the S donor resonance signal observed for samples (a) and (b).

Our results evidence that the majority of transmuted Ge atoms is active as donors on Ga sites. If Ge_P acceptors ($E_A = E_V + 258$ meV [6]) would become active in Ge_{Ga}–Ge_P DAP processes, near-edge emission should be detected. This is not confirmed by our PL data, thus supporting the conclusions of Huber et al. [1] for NTD GaP and Satoh et al. [7] for NTD GaAs that the major part of the transmuted Ge enters the Ga sites.

The distinct shift (~ 200–250 meV) of the two PL bands from 1.5 and 1.7 eV (for LEC GaP:S) to

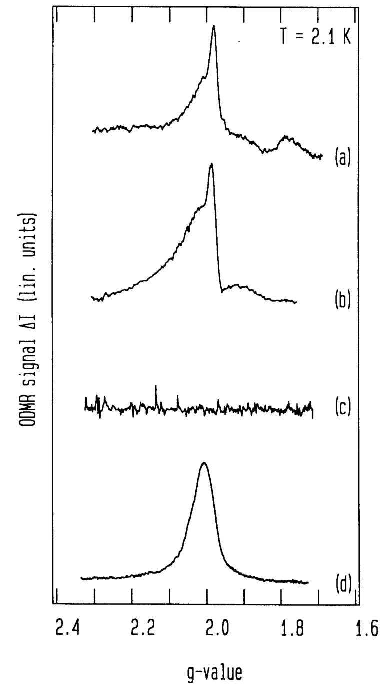

Fig. 2. ODMR spectra measured at 2.1 K of (a) the starting material LEC GaP:S. (b) annealed (800 °C, 1 h), (c) as-irradiated and (d) irradiated and subsequently annealed (800 °C, 1 h). Changes of the total infrared emission (ΔI) under 514.5 nm Ar^+ excitation are plotted against g-value.

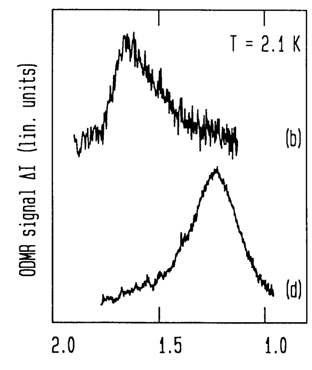

Fig. 3. Spectral dependence of the donor ODMR signals for (b) the starting material LEC GaP:S annealed (800 °C, 1 h) and (d) irradiated and subsequently annealed (800 °C, 1 h). Spectra are measured at 2.1 K with a 1.5 m monochromator and a Ge detector.

1.25 and 1.52 eV (for NTD GaP) – see fig. 1 – is a factor of two larger than the one expected to result from the change of donor ionization energy only ($E_D = 107$ meV for S_P, $E_D = 204$ meV for Ge_{Ga} [6]). This confirms previous observations [5,8] that the acceptor energy level depends on the donor impurity introduced into the sample. On the basis of PL studies of GaP doped with chalcogenides (S, Se, Te) Dishman et al. [8] proposed that the actual donor species present in the material also participates in the formation of an acceptor. The deep acceptor (at $\sim E_V + 0.7$ eV) active in the 1.5 eV DAP transition was tentatively identified as a complex incorporating a gallium vacancy (V_{Ga}) and two donors (e.g. V_{Ga}–2 S_P). The V_{Ga}–3 donor complex was tentatively proposed as the neutral complex binding an exciton [8]. The 1.52 eV band in our NTD sample is most probably of the same origin as the 1.7 eV PL observed for GaP doped with chalcogenides. This band cannot be due to the 1.5 eV DAP transition as in S, Se and Te doped GaP, since the ODMR signal due to S-related 1.5 eV PL is very weak. Extension of the Dishman model to our data would require that V_{Ga}–S_P acceptors present in the starting material are replaced by V_{Ga}–Ge_{Ga} defects. This would explain the low intensity of S-related 1.5 eV DAP emission in the NTD GaP. It would further imply that part of the gallium vacancies, being the dominant structural defects formed by neutron irradiation [9], is stabilized by the formation of V_{Ga}–Ge_{Ga} complex centres.

Summarizing, the observation of the Ge_{Ga}-related donor ODMR signal directly confirms successful transmutation, proving its feasibility for GaP. Additionally, NTD was also found to create deep acceptors, tentatively identified as V_{Ga}–Ge_{Ga} complexes. This self-compensation of NTD GaP is disadvantageous and does not occur in the case of Si and GaAs. Finally, it was found that PL intensity variations across the sample are much smaller for NTD GaP than for GaP:S before irradiation. This indicates a significant improvement of sample doping homogeneity, which is promising for possible applications in GaP technology.

Acknowledgement

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