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ANTISITES DEFECTS IN GaP*

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ESR, optical, and transport measurements were done on neutron-irradiated GaP crystals subjected to thermal annealing. The behavior of two dominant paramagnetic defects: phosphorus antisite PP_4 and WA1 [1] was followed. ESR signal similar to WA1 was earlier attributed to the defect related with gallium antisite [2]. Our thermal annealing experiments supported such attribution. Apart from that, the obtained results indicated that two dominant absorption bands in neutron-irradiated GaP with maxima at 0.79 and 1.13 eV [1] were not connected with PP_4 or WA1 defects. However, one of these paramagnetic defects (or two of them) were responsible for hopping transport in n-irradiated GaP crystals.

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Our previous studies of neutron irradiated GaP crystals provided some new experimental data [1]. First of all, we have proved that phosphorus antisite created during neutron irradiation (n-irradiation) has the same nearest neighborhood as that created during crystallization — simply four phosphorus ligands (PP_4). However, the temperature dependence of ESR signal amplitude due to PP_4 defect in n-irradiated GaP was different than the one in as grown GaP. The intensity of PP_4 line for n-irradiated crystals increased with temperature increase, whereas PP_4 line in as grown GaP showed typical behavior for ESR lines — it decreased with increasing temperature. The ESR amplitude change for n-irradiated GaP was not caused by microwave saturation. Besides PP_4 defect, the ESR studies showed the existence of another defect called WA1 [1]. Its concentration was of the same order of magnitude as that of PP_4. Optical IR absorption spectrum of n-irradiated GaP crystals showed the presence of two bands with maxima at 0.79 and 1.13 eV on large background. Conduction measurements as a function of temperature indicated hopping as the dominant transport mechanism in the temperature range below 400 K.

All these experimental results lead to the questions about the origin of WA1 defect and about correlations between absorption bands, hopping conduction and

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defects detected by ESR in n-irradiated GaP. In order to answer at least part of these questions annealing of n-irradiated GaP was performed and systematic optical, ESR, and transport studies were done.

The material used for investigations was liquid encapsulated Czochralski grown phosphorus rich GaP crystals irradiated with fast neutrons of 3.7×10^{17} cm^{-2} dose in the MARIA core at Świerk. Annealing was performed under phosphorus overpressure in successive 50°C steps in the temperature range 300–600°C. After each step of annealing the crystals were measured by ESR, optical absorption, and transport techniques.

The dependencies of normalized intensities of ESR PP_4 and WA1 signals on annealing temperature are shown in Fig. 1a. These ESR amplitudes changed

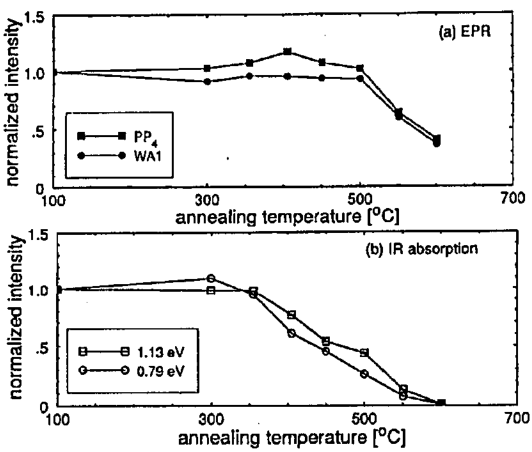

Fig. 1. Normalized intensities of (a) ESR PP_4 and WA1 signals, (b) IR absorption bands with maxima at 0.79 and 1.13 eV as a function of the annealing temperature (annealing time 30 min) for n-irradiated GaP crystals.

nearly in the same way with annealing temperature. Both defects remained at almost unchanged concentrations up to 500°C (see Fig. 1a). Above this temperature the intensity of both defects decreased. Figure 1b presents the dependencies of 0.79 and 1.13 eV absorption band intensities on annealing temperature. These dependencies followed closely each other. However, the intensity of these bands decreased starting from 350°C which differed from the paramagnetic defects behavior. These results proved that the observed absorption bands were not connected with PP_4 or WA1 defects.

One of the most important questions was the origin of WA1 defect. ESR spectrum similar to WA1 was observed earlier in plastically deformed GaP and GaAs [2]. The authors attributed this signal to the defect related to gallium antisite. Our studies brought new evidence supporting connection of WA1 with gallium antisite (Ga_P). One can expect creation of antisites at both anion and cation sites with similar concentrations during n-irradiation. Actually, it was found that during n-irradiation of GaP crystals both PP_4 and WA1 defects were created in comparable concentrations irrespective of neutron dose [1]. Additionally, Fig. 1 shows that both these defects annihilated also at the same temperature during thermal annealing of the crystal. Finally, the temperature at which PP_4 and WA1 signals started to decay was close to that of arsenic antisite created by plastic deformation or irradiation in GaAs [3].

As has been mentioned, PP_4 defect showed different temperature dependence of its ESR signal for as grown and n-irradiated GaP (see Fig. 2). For as grown crys-

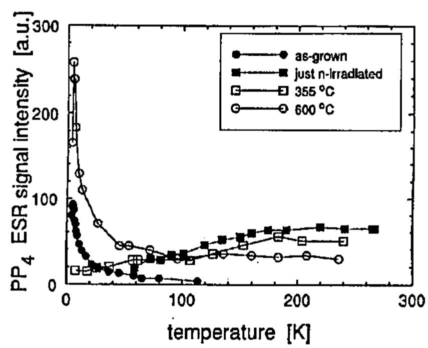

Fig. 2. ESR PP_4 signal intensities as a function of temperature for as grown and n-irradiated (before and after annealing at 355°C and 600°C) GaP crystals.

tals ESR signal amplitude had narrow maximum at 5 K associated with microwave saturation and then it decreased with increase in temperature (typical behavior of most ESR signals). After n-irradiation this behavior changed dramatically. At the lowest temperatures ESR signal was not observed and it started to appear above 50 K. Its intensity increased with temperature increase and had plateau above 180 K. Annealing of n-irradiated GaP gradually changed this behavior: the observed increase in ESR amplitude at higher temperatures progressively diminished. On the other hand, the signal started to appear at lowest temperatures, similarly to that observed in as grown material (about 5 K). ESR amplitude at about 5 K was successively higher for higher annealing temperature. The temperature dependencies of PP_4 amplitude for some annealing temperatures only are shown in Fig. 2. These temperature dependencies are not understandable at present moment and will be subjected of further studies.

Conduction measurements as a function of temperature were performed for annealed GaP crystals. The observed hopping conduction for n-irradiated crystals gradually diminished when annealing temperature decreased. But it was difficult to estimate the concentration changes of the centers responsible for transport mechanism. These difficulties arised from a lack of information about the microscopic structure of these centers, such as radius of localization. For annealed samples the temperature dependencies of conduction were proportional to $\exp((T_0/T)^{1/4})$ at lower and to $\exp(-E_3/kT)$ at higher range of temperature, similarly to non-annealed crystals [1]. During annealing the energy E_3, which described average broadening of the level taking part in hopping conduction, remained almost unchanged. The estimated value of this energy was about 0.25 eV. It was difficult to say which deep center was connected with hopping conduction. But on the other hand, only the centers having states near the Fermi level should be considered. Therefore, it was probable that hopping conduction took place between one kind of defects detected by ESR.

In summary, it was found that two absorption bands with maxima at 0.79 and 1.13 eV were not connected with PP_4 or WA1 defects. On the other hand, one of these defects (or two of them) is probably responsible for hopping transport in n-irradiated GaP. Additionally, thermal annealing experiments supported attribution of WA1 ESR signal to defect containing Ga_P.

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