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INFLUENCE OF VACANCY DEFECTS ON THE LUMINESCENCE OF GaP STUDIED BY CL AND POSITRONS

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Cathodoluminescence (CL) scanning electron microscopy and positron annihilation techniques have been used to investigate defects in electron irradiated LEC-GaP and its influence on CL emission. Defects produced by irradiation cause the quenching of green and red CL. The quenching is not related to Ga vacancies. P vacancies and other radiation defects contribute to the quenching of the green CL. Ga vacancies have been observed to anneal at 150 K.

IN A RECENT work [1] cathodoluminescence (CL) in the scanning electron microscope and positron annihilation techniques have been used to investigate the spatial distribution of vacancy defects in GaP wafers. It has been found that the profile of the vacancy concentration along the wafer diameter is the inverse of the green CL profile and has the form of the red CL profile. In the present work the mentioned techniques are used to study the relationship between the presence of high concentration of vacancies, as detected by positron annihilation, and the luminescence emission of electron irradiated GaP. The material used was S doped LEC GaP with a free carrier concentration n of $5 \times 10^{17}\,\mathrm{cm}^{-3}$. Three samples of about $6 \times 6\,\mathrm{mm}^2$ were cut from a $\{100\}$ oriented wafer. The samples were irradiated at 20 K with electrons having an energy of 2.8 MeV to a dose of $8 \times 10^{18}\,\mathrm{e}\ \mathrm{cm}^{-2}$. The isochronal annealing curve was obtained by measuring at 77 K from 77 to 600 K in 25 or 50 K intervals for heating periods of 30 min; after each annealing the positron lifetime spectrum was recorded by using a conventional coincidence system with a time resolution of 270 ps (FWHM). Additional measurements were performed at 77 K and at room temperature in unirradiated samples and in irradiated samples annealed at 700 and 925 K. The spectra were analyzed with one component after source corrections.

An irradiated sample and samples irradiated and subsequently annealed in argon atmosphere at 700 and 925 K respectively were used for the CL observations. The samples were observed in a Cambridge S4–10 scanning electron microscope at 30 kV, at temperatures between 300 and 100 K, in the emissive and CL modes. The experimental method for CL measurements in the range 350–850 nm has been previously described [2].

The CL at room temperature spectrum of the unirradiated samples shows a green band centered at about 563 nm when the electron beam is focused on the sample. With a defocused beam a spectrum showing an intense red band at 732 nm at room temperature is obtained [1]. The position of the red band depends on the observation temperature and is influenced by thermal treatments [3]. In the as-irradiated sample and in the sample annealed at 700 K after the irradiation a strong CL quenching is detected so that CL spectra cannot be recorded. In the sample annealed at 925 K some CL recovery is observed especially of the red emission. At room temperature with a focused electron beam in the scanning electron microscope a very weak green band (563 nm) is observed while with a defocused beam the red band peaked at about 705 nm, shown in Fig. 1, is recorded. At 95 K two bands, at 600–620 nm and 700 nm respectively (Fig. 2) — whose relative intensities depend on the focusing conditions — are detected. The peak of the 700 nm band shifts about 10–15 nm towards longer wavelengths by defocusing.

The mean positron lifetimes in the unirradiated

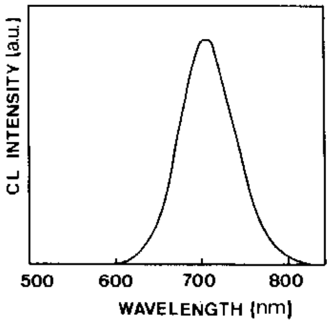

Fig. 1. CL spectrum (defocused beam) at room temperature of a sample irradiated and annealed at 925 K.

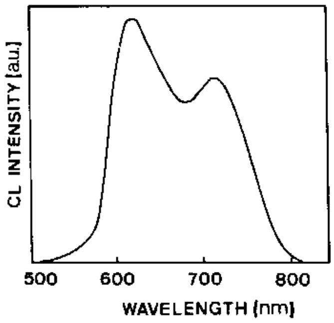

Fig. 2. CL spectrum at 95 K of the same sample as Fig. 1.

samples at 300 and 77 K are (220 ± 2) ps and (218 ± 2) ps respectively. In the irradiated samples the value of $\bar{\tau}$ at 77 K is (243 ± 2) ps. The evolution of $\bar{\tau}$, measured at 77 K, with the annealing temperature is shown in Fig. 3. The $\bar{\tau}$ values, measured at 300 K, of samples annealed at 700 and 925 K are also represented.

High energy electron irradiation produces in GaP several kinds of point defects which have been investigated by EPR [4–6], thermally stimulated current [7], infrared absorption [8] or positron annihilation [9–11]. Positron annihilation has been also used to study defects in unirradiated [12] and neutron irradiated GaP [13]. Irradiation produces vacancy type defects, as P and Ga vacancies, as well as antisites and more complex defects. The radiation induced CL quenching observed in this work agrees with a higher number of vacancies in the irradiated material. Frank and Gösele [14] have pointed out that recombination involving vacancies compete with green-band transitions and therefore the green band intensity decreases when the vacancy concentration increases. This is confirmed by combined CL and positron annihilation measurements on GaP wafers [1].

Previous positron annihilation works attribute to P vacancies the trapping of positrons in unirradiated GaP. The lifetime value for defect-free GaP is about 223 ps [1, 13]. Irradiated samples are semi-insulating and the P vacancies are positively charged and repel positrons whereas the negatively charged Ga vacancies are able to localize positrons [10, 13]. This means that the $\bar{\tau}$ value of 243 ps in our irradiated samples is due to the presence of radiation induced Ga vacancies. In Fig. 3 a decrease of mean positron lifetime with annealing temperature is observed. In the sample annealed at 700 K, the $\bar{\tau}$ value, measured at 77 K, is close and somewhat lower than the value of the unirradiated sample. The decrease of $\bar{\tau}$ below the initial value has been also observed in similar studies on irradiated GaAs [15]. Since the Ga vacancies are considered to be responsible of the radiation induced $\bar{\tau}$ increase, the observed $\bar{\tau}$ decrease by annealing may be attributed to an annealing of these defects. In electron irradiated GaAs, the Ga vacancies have been also observed to recover between 200 and 400 K [16]. The fact that the radiation induced quenching of the CL remains after the 700 K annealing indicates that Ga vacancies are not involved in the luminescence quenching mechanism. The mean positron lifetime at room temperature in the sample annealed at 700 K is 235 ps while in the unirradiated sample is 220 ps, which shows that other radiation induced point defects, as P vacancies, have not annealed out and can contribute to CL quenching. The observation of positron trapping by group V vacancies at room temperature but not at 77 K has been also found in electron irradiated GaAs [15] as well as in unirradiated GaAs [17] and could be an indication of a strong dependence of the specific trapping rate of vacancies with the temperature. The mean lifetime of the unirradiated sample has been achieved in the irradiated sample after annealing at 925 K. This suggests that the rest of the radiation induced vacancies have annealed out at this temperature. Since the disappearance of the P vacan-

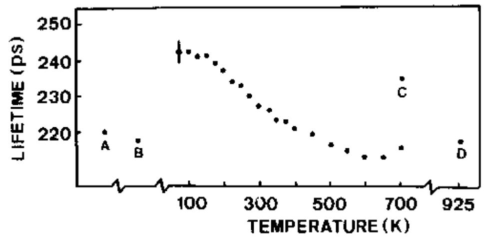

Fig. 3. Recovery of positron mean lifetime as a function of the annealing temperature in electron irradiated GaP. The points marked A and B indicate the measurements performed in the unirradiated sample at room temperature and 77 K respectively. The points marked C and D indicate the mean lifetime measured at room temperature for the irradiated samples.

cies is associated to a small recovery of the green CL, other radiation defects, in addition to P vacancies may contribute to the CL quenching.

The red CL band, contrary to the green band, has not been found to be quenched by the presence of vacancies in as-grown LEC crystals [1]. The present results show that radiation induced defects contribute to suppress the red CL band. This band recovers with annealing treatments before than the green band but remains quenched even when Ga vacancies have annealed out. It can be concluded that the presence of Ga vacancies does not either determine the red CL quenching. Annealing induced changes of the defect structure influence the red emission. Dishman *et al.* [18] have observed at 1.8 K the appearance of a new luminescence band at 600 nm, whose intensity rapidly decreases by increasing observation temperature, by annealing LEC GaP:Te 6 hours at 1025 K. These authors attribute the band to an isoelectronic center involving group VI donors and Ga vacancies. The 600–620 nm observed in the present work in the sample annealed at 925 K is probably due, as the band described in [18], to a complex defect formed during annealing. In unirradiated samples an annealing at higher temperature, in our case 5 hours at 1100 K followed by slow cooling, is necessary to produce an intense emission band at 600–620 nm. The appearance of the band seems to be favoured by the presence of radiation induced defects.

In summary, defects produced by irradiation with 2.8 MeV electrons cause the quenching of the green and red CL bands of GaP. Positron lifetime measurements show that the quenching is not related to Ga vacancies. P vacancies and other radiation defects contribute to the quenching of the green CL. Annealing the irradiated samples at 925 K produces complex defects which are involved in a CL band at 600–620 nm.

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