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Characterisation of vacancy-like defects in III–V compound semiconductors using positron annihilation technique

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Abstract. Single crystals of GaP and InSb were irradiated by 3 MeV electrons at 20 K to a total dose of $4 \times 10^{18}\, e^-/cm^2$. Isochronal annealing in the temperature region 77–650 K followed the irradiation. In GaP, the positron lifetime measurement indicated the presence of irradiation-induced vacancies in the Ga-sublattice. The vacancies disappeared at two stages observed in temperature ranges 200–300 and 450–550 K. In InSb the positron lifetime was found to increase by 8 ps compared to that in as-grown crystals (i.e. 282 ± 2 ps) after irradiation. The increase indicated the presence of irradiation-induced defects; the crystal was found to recover until 350 K with a sharp annealing stage at 250–350 K.

Keywords. III–V compound semiconductors; positron annihilation technique; vacancy-like defects; irradiation induced defects.

1. Introduction

The study of the electronic structure of materials is of fundamental importance in materials science. Throughout the last half-century great efforts have been made to devise increasingly sophisticated and accurate methods to predict the electronic structure of crystalline solids.

In recent years increasing attention has been paid to the study of defect properties in semiconducting materials as the semiconducting properties are extremely sensitive to the presence of defects and semiconductors are widely used in modern electronics and space research.

In compound semiconductors e.g. III–V compounds the presence of impurities and point defects can introduce deep levels (Von Bardeleben 1986) and the nature of defects becomes more complex due to the interaction of the intrinsic defects (vacancies, interstitials, antisites) with various impurities present in the materials. It is therefore necessary to identify these defect structures and to observe their recovery behaviour.

Among several other techniques positron annihilation has been established as one of the most efficient methods for the study of the electronic structure of crystalline solids. It has also been successfully employed to characterise the nature of defects in the materials.

Positron–electron annihilation occurs when energetic positrons emitted from a suitable radioactive isotope enter the material and thermalise. In the presence of defects positrons get trapped at the defect sites and the lifetime of positron reflects the electron density at the positron site. Generally these defects are produced in the materials by different methods such as temperature, pressure and particle irradiation.

In III–V compound semiconductors several studies have been made for the microscopic identification of native defects (Stucky *et al* 1985; Dannefaer and Kerr 1986; Dlubek *et al* 1986) as well as the observation of the annealing behaviour of radiation induced defects (Hautojarvi *et al* 1986; Sen Gupta *et al* 1986; Dlubek *et al* 1986b, 1987) with the help of the positron annihilation technique. Compared to other III–V compounds there exist few studies of defect properties in GaP and InSb.

Hence, in the present paper, results on the positron trapping at vacancy defects in GaP and InSb introduced by electron irradiation have been reported. The characterisation of vacancies and their annealing behaviour are also discussed.

2. Experimental

The samples for the present study were undoped, *n*-type GaP single crystals of dimension $5 \times 3 \times 0{\cdot}5\,mm^3$ with an initial carrier concentration of $2 \times 10^{16}\,cm^{-3}$ and *n*-type InSb single crystals of dimension $5 \times 5 \times 0{\cdot}5\,mm^3$ with an initial carrier concentration of $2 \times 10^{14}\,cm^{-3}$.

Prior to the irradiation, GaP specimens were annealed at 900 K for 2 h in an argon atmosphere in order to reduce positron trapping in as-grown defects. As-grown InSb specimens were isochronally annealed from 77–650 K at intervals of 50 K before irradiation. After annealing at each set temperature for 30 min positron lifetime was measured at 77 K in order to observe the recovery behaviour of as-grown defects.

GaP and InSb specimens were separately irradiated by 3 MeV electrons from a Van-de-Graaff accelerator at CEN–Grenoble to a dose of $4 \times 10^{18}\,e^-/cm^2$. The samples were placed in a liquid hydrogen cryostat for maintaining the temperature at 20 K during irradiation. After irradiation, the specimens were transferred at 77 K to a liquid N_2 cryostat and an isochronal annealing treatment was performed in the temperature region 77–650 K at intervals of 25 K and annealing time 30 min. The stability of the set temperature was better than $\pm 0{\cdot}3$ K. Positron lifetime measurements were performed using a ^{22}Na positron source evaporated on a thin Ni foil of thickness $1{\cdot}0\,\mu$ and all measurements were carried out at 77 K following in-situ annealing at each set temperature.

A conventional slow–fast coincidence system of resolution 280 ps (FWHM) for ^{60}Co prompt source at the experimental positron window setting was used for positron lifetime measurements. After proper source corrections all lifetime spectra were analysed by using only one exponential component. The variance of fit was maintained within 1 and there was no need for a second lifetime component.

3. Results and discussion

3.1 *GaP*

3.1a *Pre-irradiation*: The positron lifetime value obtained before irradiation was 225 ± 2 ps. This value corresponds to the lifetime values obtained also after post-irradiation isochronal annealing above 550 K. Hence it can be assigned to the positron lifetime in the bulk material (τ_b) and it agrees with the value obtained earlier by Dlubek *et al* (1986b).

Moreover, the present value ($\tau_b = 225 \pm 2$ ps) lies in between the experimental bulk lifetime values for Si ($\tau_b = 220$ ps) (Dannefaer *et al* 1986) and Ge ($\tau_b = 228$ ps) (Moser *et al* 1985).

3.1b *Post-irradiation*: Figure 1 shows the isochronal annealing curve for electron irradiated GaP in the temperature region 77–650 K. The average lifetime τ_m has been plotted against the annealing temperature. A single component fit of the lifetime data gives a lifetime value of 240 ± 2 ps in irradiated GaP at 77 K. This is high compared to the bulk lifetime τ_b, showing positron trapping at vacancy defects.

Annealing is continuous, but there are indications of two stages at temperatures 200–300 K and 450–550 K, respectively. Beyond 550 K, the average lifetime reaches the bulk value implying the disappearance of positron trapping centres.

As positrons are positively charged they can be attracted by neutral or negatively charged vacancies, whereas positively charged vacancies repel them. Hence, positrons are sensitive to the change in the vacancy charge state which is due to the shift in the Fermi level positions.

In analogy with GaAs, we assume that in GaP the vacancy at the Ga-site (V_{Ga}) is of the acceptor type and can exist in neutral or negatively charged states whereas the vacancy at the P-site (V_P) is of the donor type and can be in neutral, negative or positive states, depending on the position of the Fermi level (Das Sharma and Madhukar 1981; Mooney and Kennedy 1984). Positron-trapping is therefore dependent on the charge state of V_P, as a positively charged P-vacancy is unable to trap a positron. In *n*-type materials V_P is neutral or negatively charged, whereas in *p*-type or in semi-insulating materials V_P becomes positively charged.

After heavy irradiation at a high dose of $\Phi = 4 \times 10^{18}\, e^-/\text{cm}^2$, the specimen becomes semi-insulating independent of its original state, and the Fermi level lies in the midgap position. Therefore, after irradiation the trapping of positrons must occur due to defects involving Ga-vacancies, as only the Ga-vacancy (V_{Ga}) remains neutral or negatively charged even in semi-insulating materials.

The results in figure 1 and the average lifetime value $\tau_m = 240 \pm 2$ ps in the as-irradiated state are based on one exponential fit. It is, however, not certain that after irradiation positron-trapping in Ga-vacancies is saturated. Dlubek *et al* (1986b) found in as-grown GaP crystals a second lifetime component $\tau = 290$ ps which they attributed to As-vacancies. After neutron irradiation the same authors found $\tau = 250$ ps which was attributed to Ga-vacancies. The latter value is comparable to our value of 240 ps. Since neutron irradiation can also create some multiple vacancies we may conclude that positron lifetime in a Ga-vacancy in GaP

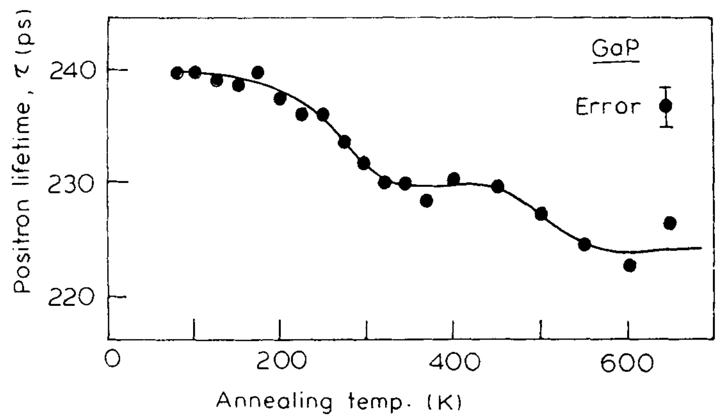

Figure 1. Variation in the positron lifetime in GaP with annealing temperature.

is $\tau(V_{Ga}) = 240$–250 ps. For comparison, in GaAs the lifetime $\tau(V_{Ga}) = 260$ ps, and $\tau_b = 230$ ps (Hautojarvi *et al* 1986). Thus in both GaP and GaAs $\tau(V_{Ga}) \simeq 1{\cdot}1\ \tau_b$.

Annealing behaviour in the present investigation shows a recovery stage between 200–300 K. This coincides with the annealing between 200–350 K that has been observed in a similar experiment in e^--irradiated GaAs and that has been assigned to Ga-vacancies (Hautojarvi *et al* 1986). The recovery stages found after room temperature neutron irradiations are above 600 K (Dlubek *et al* 1986b), where the present sample has already fully recovered. Barnes (1972) found annealing stages at 200, 300, 600 and 800 K by electrical measurements in GaP after low-temperature neutron irradiation. His first three stages overlap with the temperature region where the recovery of Ga-vacancies is observed.

3.2 *InSb*

3.2a *Pre-irradiation*: The positron-lifetime values obtained before irradiation during isochronal annealing are shown in table 1. One can see that the lifetime stays constant (282 ps) within 2 ps indicating that positrons do not see the annealing of possible native defects. Either the defect-concentration is below $10^{16}/cm^3$ or they do not trap positrons. The present value is slightly higher than that reported earlier for InSb (Sen Gupta *et al* 1986). It is also distinctly higher than in other III–V compounds (Dlubek and Brummer 1986). However, InSb has a large lattice constant. Puska (1989a) has calculated the bulk lifetimes in various semiconductors. His results are in good agreement with experiments and his estimate for InSb is 290 ps. Thus it may be concluded that the experimental lifetime value $\tau = 282$ ps is at the level expected for the positron bulk lifetime in InSb.

3.2b *Post-irradiation*: Figure 2 shows the isochronal annealing curve after electron irradiation in the temperature region from 77 K to 600 K. At 77 K a lifetime value of 290 ± 2 ps is measured, slightly higher than the lifetime of 282 ps measured before irradiation. This increase can be attributed to positron trapping at irradiation-induced vacancy defects.

The defects recover until 350 K at which temperature the pre-irradiation value at 282 ps is reached again. There are indications of a sharp annealing stage at 250–350 K.

Above 350 K the lifetime stays constant within experimental accuracy. No

Table 1. Positron lifetime in as-grown *n*-type InSb after isochronal annealing at various temperatures.

Temperature (K)	Lifetime (ps)
300	282 ± 2
400	283 ± 2
450	283 ± 2
500	282 ± 2
550	281 ± 2
600	283 ± 2
650	283 ± 2

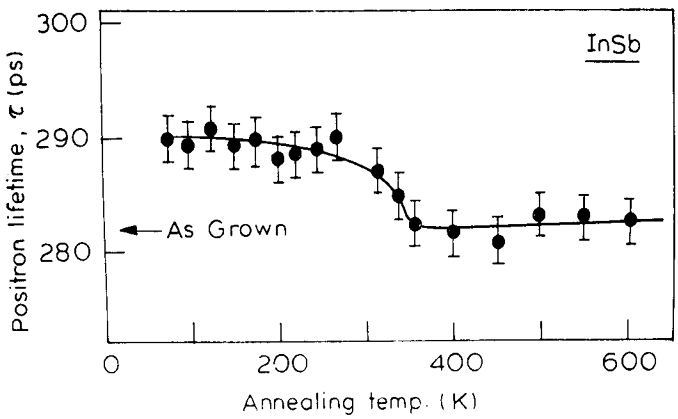

Figure 2. Variation in the positron lifetime in InSb during isochronal annealing treatment.

significant evidence of defect clustering as found by Brudnyi *et al* (1982) in InP or reverse annealing seen by Vook (1964) is present.

With another facility annealing has been studied between 20 and 77 K; no recovery at this temperature region is found.

The temperature region of positron lifetime recovery agrees well with that found by Eisen (1961, 1966). His Hall coefficient and electrical conductivity measurements in 1 MeV electron-irradiated InSb revealed four well-defined annealing stages below room temperature with the recovery completed at 320 K.

The lifetime increase of 8 ps due to irradiation is rather small. In other III–V compounds it is typically 15–25 ps. The saturation of positron trapping is perhaps not reached at 77 K because of efficient non-vacancy-type shallow traps. It is also possible that the pre-irradiation and post-annealing value of 282 ps does not correspond to the bulk, but this sounds more unlikely.

It is interesting to note that the observed recovery between 77 and 350 K is similar to that found in GaAs (Hautojarvi *et al* 1986), in GaP (Sen Gupta *et al* 1989) and in InP (Dlubek *et al* 1987). In GaAs and GaP this recovery was attributed to Ga vacancies. The same analogy suggests that the present recovery as well as that in InP (Dlubek *et al* 1987) might be due to In vacancy. To verify this, more information on the charge states of the vacancies is needed. Theoretical work on this is now in progress (Puska 1989b).

4. Conclusion

In the case of irradiated GaP the recovery of Ga vacancy defects probably occur in two stages between 200–300 K and 450–550 K. However it is difficult to say whether the defects are isolated Ga-vacancies or associated to some other defects.

In as-grown InSb crystals the positron lifetime has been obtained as 282 ± 2 ps which is proposed as the bulk lifetime value. After irradiation the lifetime has been increased by 8 ps and the original value has been recovered beyond 350 K in the same way as in other III–V compounds.

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