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Defects in ZnS and ZnSe investigated by positron annihilation spectroscopy

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Abstract. Positron lifetime measurements have been performed on as-grown and electron-irradiated single crystals of the wide-gap compound semiconductors ZnS and ZnSe. The temperature dependence of the positron lifetime in as-grown samples reveals the presence of certain grown-in defects which act as shallow positron traps. No evidence for positron trapping at room temperature is found in as-grown crystals. The values of 230 ± 3 ps and 240 ± 5 ps are proposed for the bulk positron lifetime in ZnS and ZnSe, respectively.

The positron lifetime in samples electron irradiated at 320, 77 and 20 K is interpreted in terms of positron trapping at Zn vacancy-related defects and negatively charged Zn antisites. The low-temperature inhibition of the positron trapping at open-volume defects is attributed to the presence of negatively charged Zn antisites. The positron lifetime in the samples irradiated at 20 K reveals the formation of voids in ZnS and ZnSe after annealing above ~ 600 K and ~ 500 K, respectively. These voids in ZnSe appear to anneal for temperatures above 600 K.

1. Introduction

The electrical and optical properties of the wide-gap II–VI compound semiconductors such as ZnS and ZnSe appear to be controlled by intrinsic lattice defects. When these crystals are doped with electrically active impurities, intrinsic defects are created which tend to compensate the electrical effect of the impurities. This self-compensation makes it difficult to obtain both n- and p-type conductivities by conventional doping in the same compound semiconductor. The last is crucial for obtaining light-emitting devices with p–n junctions of these materials. It has usually been accepted that singly or doubly ionized anion vacancies are the defects responsible for the self-compensation (Mandel 1964, Mandel *et al* 1964, Shirakawa and Kukimoto 1980). Although extensive studies of intrinsic defects in these semiconductors have been published, the nature of the intrinsic defects responsible for their optical and electrical properties is still a subject of considerable interest (Riehl 1981, Baltrameyunas *et al* 1985, Pecheur *et al* 1985). In addition there are experimental results that point out residual impurities as being the dominant defects in determining the conduction characteristics in as-grown ZnSe crystals (Dean *et al* 1981).

Anion vacancies seem to be the more plausible non-stoichiometric defects in ZnS and ZnSe. Optical absorption and emission bands attributed to these defects

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have been reported when these crystals are additively coloured as well as electron or neutron irradiated (Leutwein *et al* 1967, Bryant and Manning 1972a, Matsuura *et al* 1975, 1987a–c, Kishida *et al* 1986, 1988). There are reasons to think that anion vacancies in ZnS and ZnSe are usually positively charged centres. An electron paramagnetic resonance (EPR) signal, ascribed to singly ionized anion vacancies (F^+ centres) in ZnS and ZnSe, appears to be tightly correlated with the absorption and emission bands attributed to defects induced by additive colouration and electron or neutron irradiation (Schneider and Räuber 1967, Matsuura *et al* 1987d, Gorn *et al* 1990). Cation vacancies in ZnS and ZnSe, and some associated defects, have been detected by EPR and luminescence (Bryant and Manning 1972b, Corbett *et al* 1981, Taguchi and Yao 1984).

Positron annihilation spectroscopy, as a technique capable of determining unambiguously the vacancy nature of a defect, can help to reveal the role and characteristics of intrinsic defects in ZnS and ZnSe. In the present paper, positron lifetime experiments in as-grown, electron-irradiated and annealed single crystals of ZnS and ZnSe are reported. The experimental details are described in section 3. The results for ZnS and ZnSe are presented in sections 3 and 4 respectively and are discussed in sections 5, 6 and 7. Section 5 concerns the positron traps in as-grown crystals; sections 6 and 7 deal with the positron traps in crystals electron irradiated at 320 K and at low temperatures respectively. Finally the conclusions are presented in section 8.

2. Experimental procedures

Positron annihilation experiments were made on pairs of identical monocrystalline disks, ø8 mm and ~ 1 mm thick, cut from melt-grown undoped single crystals of ZnS and ZnSe. The crystals were purchased from Karl Korth (Kiel, Germany). Positron lifetime measurements were performed on several pairs of as-grown crystals. Afterwards, a pair was isochronally annealed in vacuum for 30 min in 30 K steps up to 1175 K, and measured again at room temperature after each annealing step. Another pair of as-grown samples, set into a closed-cycle cryostat, were measured in the temperature range 8–320 K. In addition, three other pairs of ZnS and ZnSe samples were electron irradiated at 320, 77 and 20 K respectively. The irradiations at 320 K were made with 1.8 MeV electrons up to a dose of 4.2×10^{17} e^- cm^{-2}. The pairs irradiated at 320 K were set into a cryostat and their positron lifetime spectra measured over the temperature range 8–320 K. The samples irradiated at 77 K were exposed to 2.5 MeV electrons up to a dose of 2×10^{17} e^- cm^{-2}. The pairs of samples irradiated at 20 K received a dose of 7.6×10^{18} e^- cm^{-2} from an electron beam of 3.0 MeV. The samples irradiated at low temperatures were stored in liquid nitrogen until measuring. These samples were isochronally annealed for 4 h inside the cryostat and the positron lifetime measured successively at the annealing temperature, i.e. during annealing, and at 77 K after each annealing step. The treatments and measurements above 500 K were performed outside the cryostat.

As-grown crystals at room temperature showed a semi-insulating behaviour. Transport measurements for determining the conduction characteristics of the electron-irradiated samples were not made.

A spectrometer with a time resolution of 245 ps (FWHM) was used for the positron lifetime measurements of the samples irradiated at low temperatures. The rest of the measurements were made with a different spectrometer having a time resolution of

300 ps. Two different ^{22}Na positron sources of about 6×10^5 Bq, deposited on a thin Ni foil, were used.

The lifetime spectra were analysed with the computer program POSITRONFIT (Kirkegaard and Eldrup 1974) taking into account two source corrections due to the contribution of positrons annihilating in the positron source. These corrections and the time resolution of the spectrometers were determined from the lifetime spectrum analyses of several reference samples. The applied source corrections were: 5.3% of 180 ps and 6.3 or 7.8% of 470 ps for ZnS, and 7.3% of 180 ps and 6.3 or 7.8% of 470 ps for ZnSe; the intensity of the long-lived correction changed from one source to the other. The source corrections were practically temperature independent. The number of counts accumulated in the spectra was typically 0.8×10^6.

3. Results in ZnS

3.1. As-grown and annealed samples

All positron lifetime spectra of the as-grown crystals are satisfactorily fitted by a single exponential term. These single-component spectra are characterized by the decay rate of their exponential term, $\lambda = \tau^{-1}$, where τ is the positron lifetime in the pair of samples. Curve (a) in figure 1 shows the positron lifetime τ as a function of temperature T in a pair of as-grown samples. The temperature dependence of τ reveals the existence of positron trapping at low temperatures. The decrease of τ in two stages suggests the presence of two effective positron traps at low temperatures.

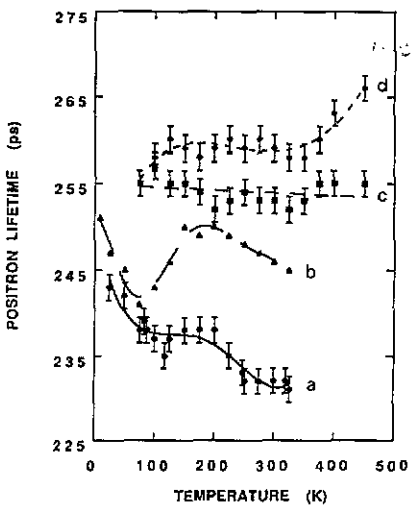

Figure 1. Positron lifetime as a function of temperature in ZnS: (a) as-grown samples, (b) and (d) samples electron irradiated at 320 K and 77 K respectively. Curve (c) shows the positron lifetime, measured at 77 K, versus annealing temperature in samples irradiated at 77 K.

The measurements performed at room temperature (RT) on different pairs of as-grown samples resulted in a positron lifetime around 230 ps. Isochronal annealing up to 1175 K does not produce any significant change in the τ value. An average value of 230 ± 3 ps is found for the lifetime of the as-grown and annealed samples.

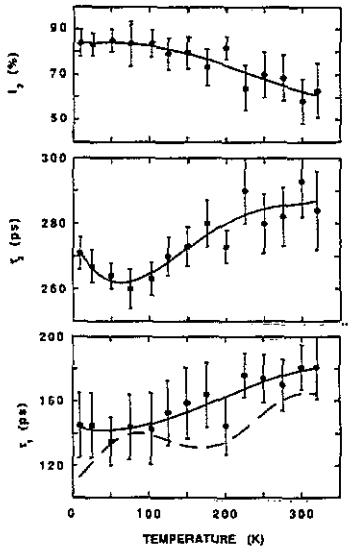

Figure 2. Positron annihilation parameters, obtained from unconstrained two-component analyses, as a function of temperature in ZnS electron irradiated at 320 K. The broken curve shows the trend of the τ_1 values calculated assuming a two-state trapping model.

3.2. Samples electron irradiated at 320 K

In this case the spectra could be satisfactorily fitted by two exponential terms. The intensity I_2 and the lifetimes τ_1 and τ_2 of the spectral components are given as a function of temperature in figure 2. Curve (b) in figure 1 shows the mean lifetime, $\langle\tau\rangle = (1 - I_2)\tau_1 + I_2\tau_2$, versus temperature. A decrease of $\langle\tau\rangle$ is observed in the interval 8–75 K while I_2 stays constant and τ_2 tends to decrease. This decrease in $\langle\tau\rangle$ is followed by an increase succeeded by a slight and monotonous decrease for T above ~ 200 K. This last decrease appears to be accompanied by a reduction in I_2.

3.3. Samples electron irradiated at low temperatures

The spectra of the samples irradiated at 77 K are satisfactorily fitted by a single exponential term. Two-component analyses of these spectra yield unacceptable standard deviations or inconsistent values for the annihilation parameters. Curves (c) and (d) in figure 1 show the positron lifetime, measured at 77 K after annealing and at the annealing temperature respectively. The lifetime at 77 K, τ, remains constant at 254 ± 2 ps. Also the lifetime at the annealing temperature, τ_T, stays constant at 258 ± 2 ps for temperatures $100 \leqslant T \leqslant 350$ K. For temperatures above ~ 375 K, it appears to increase.

The results obtained for samples irradiated at 20 K are shown in figure 3. Their spectra are very well adjusted to a single exponential term, with the exclusion of the spectra measured at 77 K after annealing at $T \geqslant 650$ as well as those measured during annealing at $T \geqslant 400$ K which are two-component. The mean positron lifetime $\langle\tau\rangle$ of these two-component spectra is represented in figure 3. Their annihilation parameters obtained from two-component analyses are given in table 1. It is found that the positron lifetime at the annealing temperature, curve (b), increases monotonously in the interval 100–500 K. However, the lifetime measured at 77 K after annealing

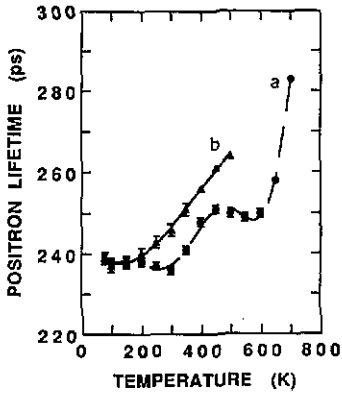

Figure 3. Positron lifetime versus annealing temperature in ZnS electron irradiated at 20 K. Curve (a) indicates the lifetime values measured at 77 K after isochronal annealing, and curve (b) the values measured at the annealing temperature.

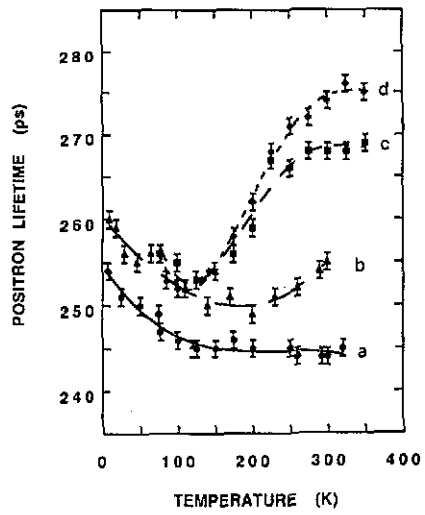

Figure 4. Positron lifetime as a function of temperature in ZnSe: (a) as-grown samples, (b) and (d) samples electron irradiated at 320 K and 77 K respectively. Curve (c) shows the positron lifetime, measured at 77 K, versus annealing temperature in samples irradiated at 77 K.

Table 1. Positron annihilation parameters in ZnS electron irradiated at 20 K obtained from two-component analyses.

Annealing temperature (K)	τ_1 (ps)	τ_2 (ps)	I_2 %	$\langle\tau\rangle$ (ps)	τ_b (ps)
Measured at the annealing temperature					
400	183±39	270±8	84±10	256	251
450	115±16	278±2	89.6±1.6	261	242
500	167±12	300±4	73±4	264	247
Measured at 77 K after annealing					
650	218±7	343±16	32±8	258	247
700	228±3	449±11	25±2	283	260

increases in two stages in the interval 300–700 K, curve (a). Recovery of the lifetime is not observed for annealing at $T \leqslant 700$ K.

4. Results in ZnSe

4.1. As-grown and annealed samples

The as-grown ZnSe crystals yielded a single-component spectrum. Curve (a) in figure 4 shows the temperature dependence of τ in a pair of as-grown samples. This de-

pendence makes evident the presence of grown-in defects which are effective positron traps at low temperatures. Isochronal annealing at $T \leqslant 1175$ K did not induce any significant change in τ. From the measurements performed on several pairs of as-grown and annealed samples, an average value of 240 ± 5 ps is obtained for the positron lifetime at room temperature.

4.2. Samples electron irradiated at 320 K

Curve (b) in figure 4 shows the τ value, obtained from single-component analyses, versus measuring temperature for ZnSe irradiated at 320 K. The two-component fits of these spectra yielded inconsistent parameters or unacceptable variances. A continuous decrease of τ with increasing temperature for $T < 200$ K, followed by an increase, is observed.

4.3. Samples electron irradiated at low temperatures

The lifetime spectra of the samples irradiated at 77 K appear to be single component. A two-component fit of these spectra was tried, but it resulted in unacceptable standard deviations and a large dispersion in the annihilation parameter values. The results are given in figure 4; curves (c) and (d) respectively show the positron lifetime measured at 77 K after annealing, τ, and at the annealing temperature, τ_T, as a function of annealing temperature. After an initial decrease, τ increases after annealing at $T > 125$ K, resulting in a constant value of 268 ± 2 ps for annealing in the temperature range $225 < T \leqslant 350$ K. τ_T starts to increase monotonously for $T > 100$ K.

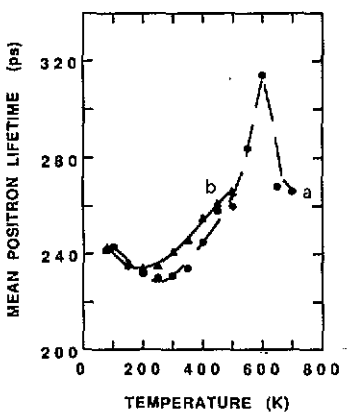

Figure 5. Mean positron lifetime versus annealing temperature in ZnSe electron irradiated at 20 K. Curve (a) indicates the $\langle\tau\rangle$ values measured at 77 K after isochronal annealing, and curve (b) the values at the annealing temperature.

The results obtained for ZnSe irradiated at 20 K differ remarkably from those for samples irradiated at 77 K. All spectra, measured at 77 K or during annealing at $T > 77$ K, are very well fitted by two exponential terms. Single-component analyses yield unacceptable variances. The annihilation parameters obtained from unconstrained two-component analyses are given in figures 5, 6 and 7. The mean lifetime at 77 K after annealing $\langle\tau\rangle$, and at the annealing temperature $\langle\tau_T\rangle$, are shown in figure 5. Figures 6 and 7 show the parameters τ_1, τ_2 and I_2 measured at 77 K and at the annealing temperature respectively. For $T < 200$ K, the $\langle\tau\rangle$ and

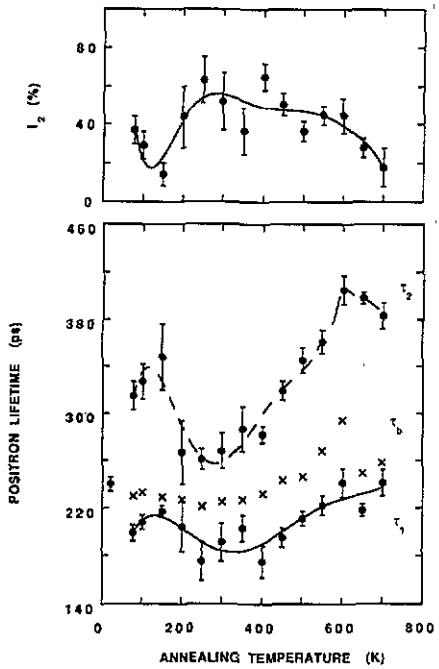

Figure 6. Positron annihilation parameters, obtained from unconstrained two-component analyses, versus annealing temperature in ZnSe electron irradiated at 20 K. The measuring temperature is 77 K. The points (×) denote the τ_b values calculated by equation (2), and (♦) indicates the bulk positron lifetime attributed to ZnSe.

$\langle \tau_T \rangle$ values coincide. After an initial decrease with temperature, $\langle \tau \rangle$ and $\langle \tau_T \rangle$ reach their minimum values at $\simeq 250$ K and $\simeq 200$ K respectively. $\langle \tau \rangle$ then increases up to a maximum value of 314 ps after annealing at 600 K, after which it decreases after annealing at 650 K. The temperature dependences of the annihilation parameters τ_1, τ_2 and I_2, measured at 77 K and at the annealing temperature, are qualitatively similar as seen in figures 6 and 7.

It should be mentioned that for the 20 K irradiated samples, a three-component analysis of the spectra obtained at 77 K, after annealing at $T \geqslant 600$ K, yields a slightly better variance than the two-component one. A faint long-lived component, $1.1 \leqslant \tau_3 \leqslant 1.8$ ns, appears in these spectra but not in the rest of the spectra. This long-lived component is so faint, $I_3 \simeq 0.2$–0.3%, that the differences between the annihilation-parameter values obtained from the respective two- and three-component analyses are within their standard deviations. The annihilation parameters $\langle \tau \rangle$, τ_1, τ_2 and I_2 for these spectra, shown in figures 5 and 6, were obtained from a two-component analysis after subtracting the long-lived component. The origin of this component, which most likely is not spurious, will be discussed later.

5. Positron traps in as-grown crystals

The decrease of τ with T in the temperature range 8–320 K may be attributed either to a decrease of the trapping coefficient or to a thermally activated positron detrapping from shallow traps. Also, a gradual disappearance of the positron trapping, due to a thermally activated change in the charge state of the traps, could be invoked.

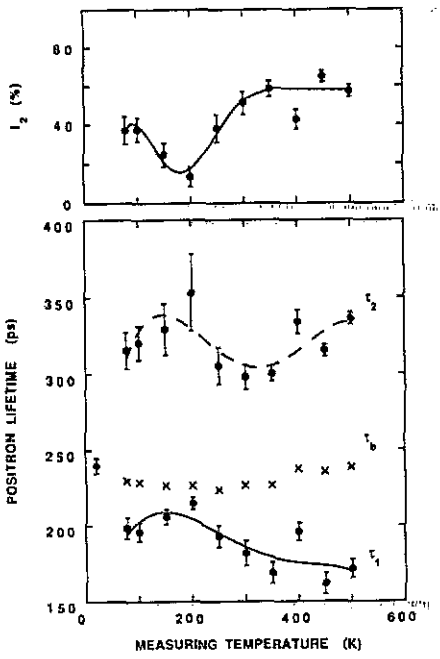

Figure 7. Positron annihilation parameters, obtained from unconstrained two-component analyses, as a function of temperature in ZnSe electron irradiated at 20 K. The points (×) denote the τ_b values calculated by equation (2), and (♦) indicates the bulk positron lifetime attributed to ZnSe.

Anion vacancies in ZnS and ZnSe, which are doubly ionized donor centres, are expected to be effective positron traps in the neutral state but not when they are ionized, i.e. positively charged in regard to the lattice; the same behaviour would be expected for other anion vacancy-related donor centres. On the contrary, Zn vacancies in these crystals are acceptor centres and therefore can be effective positron traps when they are ionized. The same would happen to any Zn vacancy-related acceptor centre. We rule out the anion vacancies as the grown-in defects responsible for the observed low-temperature trapping because the presence of these defects in ZnS and ZnSe has only been reported in additively coloured or irradiated crystals. Moreover, anion vacancies have been shown to appear as F^+ centres in these samples (Schneider and Räuber 1967, Matsuura *et al* 1987d, Gorn *et al* 1990). Therefore it seems that the observed temperature dependence of τ cannot be attributed to low-temperature trapping at neutral anion vacancies, i.e. F centres.

It can be accepted that the decrease of τ with T is due to a decrease of the trapping coefficient only if the traps are negatively charged vacancies (Puska *et al* 1990). The plausible vacancies negatively charged in ZnS and ZnSe are ionized Zn vacancies and their associated defects. Since the τ values at RT for the as-grown samples are the same as those for the samples annealed at 1175 K, it is reasonable to suppose that there is no room-temperature trapping at these defects. If there were trapping, the thermal annealing should reduce the concentration of the positron traps, and a decrease in the τ value would be observed. Thus it seems reasonable to accept that the defects responsible for the low-temperature trapping are shallow positron traps. Two types of shallow traps can be considered in the as-grown crystals: (i) negatively charged acceptor centres with no open volume such as residual impurities or antisites (Saarinen *et al* 1989), and (ii) open-volume defects such as dislocations, intrinsic stacking faults or inversion twin boundaries, and twin-

boundary jogs. The significant increase of τ with decreasing temperature suggests that the shallow traps are open-volume defects. Transmission electron microscopy has revealed that the dominant grown-in defects in ZnS and ZnSe are thin twins. These twins usually appear in small groups and present frequent twin-boundary jogs decorated by numerous defects (Mizera *et al* 1984, Qin *et al* 1986). These jogs or their associated defects can act as shallow positron traps. Also, negative (1 1 1) inversion twin boundaries, which may be present in ZnS and ZnSe (Austerman and Gehman 1966, Shiojiri *et al* 1982), could be effective positron traps at low temperatures. Negative inversion twins, in addition to being of open-volume structure, are negatively charged, in principle. The positron trapping at these grown-in defects would disappear for temperatures above ~ 250 K and ~ 200 K in ZnS and ZnSe, respectively. The two-stage decrease of τ in ZnS suggests the thermal activation of positron detrapping from two types of shallow traps.

The fact that the low-temperature lifetime spectra cannot be decomposed into two components suggests that the positron lifetime at the shallow traps does not differ too much from the bulk lifetime. The analysis program of the spectra cannot resolve two components properly when their lifetime values are very close to each other.

As annealing at 1175 K does not induce any significant change in the RT value of τ, it is reasonable to assume that grown-in defects present in these melt-grown crystals are not effective positron traps at RT. Thus the average of the τ values measured at RT is tentatively attributed to the bulk lifetime, i.e. 230 ± 3 ps and 240 ± 5 ps for ZnS and ZnSe respectively.

6. Positron traps in crystals electron irradiated at 320 K

The enhancement of the positron lifetime in the samples irradiated at 320 K, with regard to that in the as-grown crystals (curves (b) in figures 1 and 2) reveals the presence of vacancy-type defects. It is expected that anion and cation vacancies in ZnS and ZnSe may be created by electron irradiation at 320 K (Bryant and Hamid 1969, Bryant and Manning 1972b, Matsuura *et al* 1987a–d, Watkins 1974, Gorn *et al* 1990). Isolated anion vacancies may be excluded as the defects responsible for the low-temperature trapping observed in ZnS and ZnSe irradiated at 320 K. They would be positively charged as F^+ centres (Bryant and Manning 1972a, Tarkpea and Ots 1985, Matsuura *et al* 1987a–d, Gorn *et al* 1990). Consequently the enhancement of τ should, in principle, be attributed to isolated Zn vacancies and/or neutral or negatively charged associated defects such as V_S–V_{Zn}, V_{Se}–V_{Zn} or V_{Zn}–impurity complexes. Isolated Zn vacancies induced by electron irradiation are stable up to ~ 393 K in ZnS (Watkins 1977). However, in ZnSe irradiated at 320 K the Zn vacancies appear as V_{Zn}^-–V_S^+ or V_{Zn}–impurity complexes (Bryant and Hamid 1969, Bryant and Manning 1972b). In addition to these electron-irradiation-induced traps, grown-in defects can simultaneously act as shallow positron traps as observed in the as-grown samples. Thus, if the electron-irradiation-induced traps are negatively charged, the initial decrease of positron lifetime with increasing temperature in ZnS and ZnSe irradiated at 320 K, can be attributed to the temperature dependence of the trapping coefficient at the irradiation-induced traps, as well as to positron detrapping from grown-in defects.

In addition, according to the model proposed by Corbel *et al* (1990) to account for the temperature dependence of the positron trapping in electron-irradiated GaAs,

electron irradiation at 320 K can produce negatively charged Zn antisites and convert residual aliovalent impurities into negative ions. Zn antisites in ZnS and ZnSe are acceptors and appear to be, along with the Zn vacancy, the dominant intrinsic defect in these crystals (Jansen and Sankey 1989). Negatively charged Zn antisites, and other negative ions created by irradiation, can act as shallow positron traps simultaneously in competition with grown-in defects and irradiation-induced Zn vacancy complexes. Positron trapping in Rydberg states weakly bound at negative ions, such as antisites or impurities, has been invoked to account for the temperature dependence of the positron trapping in semiconductors (Corbel *et al* 1990, Puska *et al* 1990). The lifetime of these states is expected to be similar to the bulk positron lifetime or even shorter.

Thus, if shallow traps such as grown-in defects and negative Zn antisites, or impurity ions, are effective positron traps in addition to the irradiation-induced Zn vacancies, the expected positron lifetime spectrum should be three- or four-component. Bloch positrons and positrons localized at the different traps would contribute to the lifetime spectrum. However, the lifetime spectra are not properly resolved into the corresponding components when the positron lifetimes at grown-in defects and at negative ions are similar to the bulk lifetime. The results for as-grown samples suggest that the positron lifetime at grown-in defects is indeed close to the bulk lifetime. Consequently, the short lifetime τ_1 obtained from the two-component analyses, figure 2, would be due to a superposition of decay rates corresponding to Bloch states, and states localized at shallow traps such as grown-in defects and irradiation-induced negative ions. The resolved long lifetime τ_2 would be tentatively attributed to positrons trapped at Zn vacancy-related defects produced by electron irradiation.

If the two-state trapping model is applied to the annihilation parameters obtained from the unconstrained two-component analyses for 320 K irradiated ZnS, the expected value for τ_1 would be given by (Saarinen *et al* 1989)

$$\tau_1 = \tau_b[1 + (\langle\tau\rangle - \tau_b)/(\tau_2 - \langle\tau\rangle)] \tag{1}$$

where τ_b is the bulk lifetime and $\langle\tau\rangle$ the mean positron lifetime. Using for τ_b the average τ obtained for as-grown and annealed samples, i.e. 230 ps, (1) yields values for τ_1 which are systematically lower than those obtained from the two-component analysis of the spectra. The broken curve in figure 2 shows the trend of the values calculated for τ_1. Also, from the two-state trapping model the τ_b value is obtained by

$$1/\tau_b = (1 - I_2)/\tau_1 - I_2/\tau_2. \tag{2}$$

We find τ_b values systematically a little higher than 230 ps. The discrepancy between the expected and measured values of τ_1, or between the calcaulted values for τ_b and the proposed one, is attributed to the contribution of positrons trapped at shallow traps to the short-lifetime component of the spectra. Also it is seen that the temperature dependence of $\langle\tau\rangle$ for $T \leqslant 75$ K cannot be exclusively attributed to an increase of the trapping coefficient at the defects responsible for the long-lifetime component. According to the two-state trapping model, the τ_1 value is given by

$$\tau_1 = (\tau_b^{-1} + \mu_d c_d)^{-1} \tag{3}$$

where the specific trapping rate μ_d is related to the trapping coefficient of the defects. Thus τ_1 would decrease for decreasing temperature if the concentration of traps c_d

remains constant. However, the measured τ_1 values do not exhibit this trend for $T \leqslant 75$ K as shown in figure 2.

In ZnS, the temperature dependence of $\langle\tau\rangle$ for $75 \leqslant T \leqslant 150$ K, curve (b) in figure 1, can be attributed to thermally induced positron detrapping from the negatively charged Zn antisites and ions induced by irradiation. The monotonous decrease of $\langle\tau\rangle$ for $200 < T \leqslant 325$ K is attributed to a Fermi-level-controlled change in the charge state of the traps responsible for the long lifetime component. If the electron-irradiation-induced enhancement of the positron trapping is due to Zn vacancy-related defects, as discussed above, the temperature dependence of $\langle\tau\rangle$ in these temperature intervals may be associated with a charge-state transition in these defects, controlled by the position of the Fermi level in the gap. In this temperature interval the τ_2 value appears to increase, figure 2. This would mean that the transition reduces the electron density at the trap. The decreasing trend of I_2 would be attributed to a decrease in the trapping coefficient. Assuming that the τ_2 values correspond to positrons trapped at Zn vacancy-related defects, the values found for $T \leqslant 125$ K could be associated with defects related with V_{Zn}^{2-} or V_{Zn}^{-} centres, and those for T around ~ 300 K would be attributed to the same defects with a lower grade of ionization. If it is assumed that after irradiation the Fermi level is at such a position that the Zn vacancies are singly ionized at RT, a value of 266 ± 5 ps is tentatively ascribed to the positron lifetime at V_{Zn}^{2-}-related defects, and $\simeq 286$ ps to positrons trapped at V_{Zn}^{-}-related defects.

For ZnSe, the increase of τ for T above ~ 200 K, curve (b) in figure 4, is also associated with positron detrapping from negatively charged Zn antisites, and other plausible negative ions, produced by electron irradiation. A transition in the charge state of the traps, similar to that proposed for ZnS, may be invoked to explain the observed temperature dependence of the positron lifetime.

7. Positron traps in crystals electron irradiated at low temperature

7.1. Crystals irradiated at 77 K

7.1.1. ZnS. The lifetime measured at 77 K, τ, remains essentially constant after annealing in the temperature range 77–450 K, curve (c) in figure 1. However, the lifetime measured at the annealing temperature, τ_T, shows a two-stage reversible increase, curve (d) in figure 1. As discussed in section 6, the electron-irradiation-induced increase of τ appears to be due to trapping at V_{Zn}- or V_{Zn}-related defects. The analysis program did not yield a reliable decomposition of the spectra, although it did in the case of 320 K irradiated crystals having a shorter positron lifetime. This could be interpreted as evidence of trapping saturation. Nevertheless the average value of τ measured at 77 K after annealing, 254 ± 2 ps, is significantly lower than the value of $\simeq 266$ ps found at 77 K for τ_2 in the 320 K irradiated samples, and tentatively attributed to V_{Zn}-related defects. This suggests that, in addition to V_{Zn}-related defects, other defects that are effective positron traps at 77 K are present in the samples. The observed lifetime of $\simeq 254$ ps would be a weighted mean value of the positron lifetime at different states. In accordance with the discussion in section 6, negatively charged Zn antisites, and ions of residual impurities, produced by irradiation can act as effective traps for temperatures below ~ 150 K. Thus the increase of τ_T with respect to τ for $T \geqslant 125$ K, curves (c) and (d) in figure 1,

would be due to thermal detrapping from these shallow traps. The average value of τ_T for $125 \leqslant T \leqslant 375$ K, 259 ps, is quite close to that of 266 ± 5 ps proposed for V_{Zn}^{2-}-related defects above. The τ_T increase for $T > 375$ K, curve (d) in figure 1, would be attributed to the conversion $V_{Zn}^{2-} \rightarrow V_{Zn}^{-}$ as proposed in section 6 to account for the transition 266 → 286 ps. This transition for the 320 K irradiated samples is accomplished in the interval 125–225 K; however, for the 77 K irradiated samples its onset appears to be shifted to ~ 375 K. This shift can be due to a change of the Fermi level position with regard to the ionization level of the defects. A lower temperature for the transition onset suggests a Fermi level position closer to the upper ionization level of the V_{Zn} centre. As the temperature increases, the Fermi level goes down, crossing the upper ionization level and inducing the transition in the charge state of the defect. The results suggest that the Fermi level position in the 77 K irradiated samples is further above the ionization levels of the V_{Zn} centre than in the case of the 320 K irradiated samples.

7.1.2. ZnSe. The results for 77 K irradiated ZnSe, curves (c) and (d) in figure 4, can be explained as follows. The recovery of the positron lifetime τ, measured at 77 K after annealing in the interval 77–125 K, is evidence of defect annealing. We attribute this recovery to recombination of Zn vacancies with Zn interstitials. The recombination of V_{Zn}–Zn_I close pairs in electron-irradiated ZnSe takes place for T below ~ 180 K (Watkins 1974). It is important to note that in the interval 77–125 K, the lifetime values measured at the annealing temperature τ_T tend to be lower than τ. The expected positron detrapping from grown-in defects for $T \leqslant 125$ K discussed in section 5, along with the recombination of V_{Zn}–Zn_I close pairs, would explain the above result. Another plausible explanation is the temperature dependence of the positron trapping coefficient at electron-irradiation-induced traps.

The irreversible increase of τ after annealing in the range $150 < T \leqslant 250$ K means that either an irreversible structural change in the traps or the formation of new traps takes place. We propose the following model: at temperatures below ~ 150 K the effective traps would be, in addition to certain grown-in defects, Zn vacancy-related defects such as V_{Zn} centres, V_{Zn}–Zn_I close pairs and V_{Zn}–impurity complexes, and negatively charged Zn antisites or impurity ions, as previously discussed. Moreover, another kind of electron-irradiation-induced defect may be considered: the association of a Zn vacancy and a V_{Se}–Se_I close pair, i.e. the V_{Zn}–V_{Se}–Se_I complex. This complex may or may not be an effective trap depending on the Fermi-level position which in turn depends on the irradiation conditions and temperature. At $T > 125$ K the Se vacancy and the Se interstitial can recombine and the complex becomes a Zn vacancy increasing the positron trapping. This would account for the increase of both lifetime τ and τ_T. These vacancies could be doubly ionized for $T < 250$ K, i.e. V_{Zn}^{2-} centres, so the reversible increase of τ_T with respect to τ found for $T \geqslant 250$ K may be attributed to the thermally induced transition $V_{Zn}^{2-} \rightarrow V_{Zn}^{-}$.

7.2. Crystals irradiated at 20 K

7.2.1. ZnS. The positron detrapping from negatively charged Zn antisites, and from other irradiation-induced negative ions, can account for the reversible increase of τ_T with respect to τ for annealing at $T \leqslant 300$ K, see figure 3. The values found for τ in this temperature range are slightly higher than the proposed bulk lifetime of 230 ps. This suggests that the predominant effective traps in this case are Zn antisites and

negative ions of residual impurities. The electron-irradiation-induced Zn vacancies seem scarcely to contribute to the positron trapping. This can occur because the Zn antisites in the 20 K irradiated samples, as double acceptor centres (Jansen and Sankey 1989), were doubly charged, i.e. as a Zn_s^{2-} centre. The positron binding energy at this centre can be strong enough to turn it into a more efficient trap than the Zn vacancies at low temperatures.

It is noted that the positron detrapping from Zn antisites can continue up to 300 K, while in the 77 K irradiated samples there is no evidence for such detrapping at temperatures above ~ 150 K, curve (d) in figure 3. This fact is attributed to their charge state. They could be singly ionized in the case of 77 K irradiated samples but doubly ionized in the 20 K irradiated samples. It would mean that the Fermi level in the 20 K irradiated samples is in a higher position than in the 77 K irradiated samples. Assuming this model, it is reasonable to find a shorter positron lifetime in the 20 K irradiated samples because the lifetime of the positron bound to a Zn_s^{2-} antisite would be shorter than the one for a Zn_s^- antisite.

For temperatures above ~ 300 K, Zn vacancies may become mobile and complex defects, such as V_{Zn}–impurity and V_s^+–V_{Zn}^{2-}, or V_s^+–V_{Zn}^-, can be produced. This would explain the increase of τ after annealing in the range $300 < T \leqslant 400$ K, curve (a) in figure 3. The increase of τ_T with respect to τ, curve (b) in figure 3, can be attributed to a charge-state transition in these complexes. Nevertheless, the two-component analyses of the lifetime spectra at 400 K and 450 K, table 1, yield a long lifetime component similar to the τ_2 values in the 320 K irradiated samples, and close to the τ_T values in the 77 K irradiated samples at the same temperatures, which have previously been attributed to V_{Zn}-related defects. This is so because, very likely, the long lifetime corresponding to the spectra at $T \geqslant 400$ K is not exclusively due to trapping at V_s–V_{Zn} divacancies. Assuming the two-state trapping model, the calculated τ_b values from the annihilation parameters summarized in table 1 show that the results are not consistent with the presence of a single trapped state in the 20 K irradiated samples.

The abrupt increase of τ after annealing at $T > 600$ K, curve (a) in figure 3, is associated with the formation of vacancy aggregates as revealed by the appearance of a long-lifetime component with a τ_2 value between 340 and 450 ps, table 1. These high values suggest that the vacancies are aggregated into tridimensional voids.

7.2.2. ZnSe. The initial decrease of τ and τ_T, observed in the 20 K irradiated ZnSe samples after annealing at $T < 200$ K, figure 5, is associated with the recombination of Zn interstitials with Zn vacancies as discussed for the 77 K irradiated samples. However, the appearance of a long-lived component with a lifetime between 315 and 350 ps, in the spectra measured at 77 K and at the annealing temperature, indicates the presence of traps with an associated volume larger than the one for V_{Zn} centres or V_{Zn}–impurity pairs. The steep decrease of τ_2 in the spectra measured at 77 K after annealing at 200 K, figure 6, suggests a structural change in the traps. The new traps responsible for the long-lifetime component after annealing at $200 \leqslant T \leqslant 400$ K appear to have τ_2 values in the range 260–287 ps, figure 6. These values are similar to that of 268 ± 2 ps found for τ in the 77 K irradiated samples after annealing at $225 < T \leqslant 350$ K, curve (c) in figure 4. Therefore, in accordance with the discussion in section 7.1.2, the τ_2 values in the range $200 \leqslant T \leqslant 400$ K are tentatively attributed to V_{Zn}^{2-} centres.

To account for the transition in τ_2 after annealing at 200 K, we propose the fol-

lowing model: in these samples there probably exist Zn_I–V_{Zn}–V_{Se} and V_{Zn}–V_{Se}–Se_I complex defects that are effective positron traps at low temperatures, in competition with other irradiation-induced defects. Trapping at these complex defects can produce the long-lifetime component of 315–350 ps found for temperatures below ~ 200 K, figures 6 and 7. Recombination of the interstitial, with its corresponding vacancy during annealing at temperatures below $\simeq 200$ K, would produce the decrease of I_2 observed in this temperature range. This recombination would transform the complexes into Se and Zn vacancies, sequentially. Se vacancies are expected not to be effective traps, as discussed previously. At temperatures below ~ 150 K, the Zn antisites can be very efficient traps if they are doubly charged, i.e. Zn_{Se}^{2-} centres, as discussed above. The thermal detrapping from the Zn antisites would account for the τ_T increase with regard to τ for $T > 150$ K, figure 5.

The τ_2 values measured during annealing at $200 < T < 400$ K appear to be ~ 300 ps, figure 7, while at 77 K after annealing in the same temperature range they are between 260 and 287 ps, figure 6. This difference suggests a thermally induced transition in the charge state of the traps responsible for the long lifetime, which is consistent with the transition $V_{Zn}^{2-} \rightarrow V_{Zn}^{-}$ proposed to account for the reversible increase of the positron lifetime found for the 77 K irradiated samples in the interval $225 < T \leqslant 350$ K, curves (c) and (d) in figure 4. This means that lifetime values of 273 ± 11 ps and ~ 300 ps would be expected for positrons trapped at V_{Zn}^{2-} and V_{Zn}^{-} centres in ZnSe, respectively.

According to Watkins (1977), isolated Zn vacancies in electron-irradiated ZnSe can be stable up to ~ 400 K and V_{Zn}–donor complex defects up to ~ 620 K. So the V_{Zn} centres would become mobile at about 400 K migrating towards the V_{Se}^{+} centres to produce V_{Zn}–V_{Se} divacancies which would be the new traps after annealing in the range $400 < T < 600$ K. Values between 320 and 360 ps are found for τ_2 measured at 77 K after annealing in this temperature interval, figure 6. These values are consistent with those of 315–350 ps obtained after annealing at $T < 200$ K, and attributed to V_{Zn}–V_{Se}–interstitial complexes. The increase of τ_2 up to ~ 400 ps after annealing at 600 K reveals the formation of defects with a large associated volume such as voids created by agglomeration of V_{Zn}–V_{Se} divacancies. Additional evidence for the formation of the voids would be the sudden appearance of the faint third lifetime component of 1.1–1.8 ns after annealing at 600 K, mentioned in section 4.3. This long-lived component is attributed to pick-off annihilation of ortho-Ps states originated inside the voids or at their internal surfaces.

It should be mentioned that the annihilation parameters obtained from two-component analyses are not consistent with a single-trap model, as the τ_b values calculated by (2) reveal, with the exception of those measured during annealing at $400 \leqslant T \leqslant 500$ K (see figures 6 and 7). The calculated τ_b values for these spectra result in values in agreement with the bulk lifetime of 240 ps proposed for ZnSe.

8. Conclusions

Positron trapping at shallow traps is found in as-grown ZnS and ZnSe single crystals. The grown-in defects responsible for this low-temperature trapping appear to be open-volume likely defects associated to intrinsic stacking faults or inversion twin boundaries. The results in as-grown and annealed samples suggest a bulk positron lifetime of 230 ± 3 ps and 240 ± 5 ps in ZnS and ZnSe respectively.

The positron-lifetime enhancement in the samples irradiated at 320 K and 77 K is attributed to trapping at Zn vacancy-related defects. However, the results are not consistent with a single-trap model. A low-temperature inhibition of the trapping at Zn vacancy-related defects is observed in the samples irradiated at 20 K. This trapping inhibition and the temperature dependence of the positron lifetime indicate the formation of positron Rydberg states localized at negatively charged Zn antisites. The isochronal annealing experiments performed on the samples irradiated at 20 K show vacancy agglomeration into tridimensional voids.

These results in ZnS and ZnSe prove that positron annihilation spectroscopy can be a valuable technique for investigating the nature of the defects and their charge state in the wide-gap compound semiconductors.

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