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Temperature effects on the positron annihilation characteristics in III–VI layered semiconductors

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Abstract. Positron lifetime and Doppler broadening measurements have been performed on the layered semiconductors GaS, GaSe and GaTe in the temperature range 8–320 K. The temperature dependences of the annihilation parameters in GaS and GaSe are analysed in terms of the thermal expansion coefficient of the lattice and a volume coefficient of the annihilation parameter. The results reveal a noticeable volume effect on the positron annihilation characteristics in the bulk of GaS and GaSe; no evidence for positron trapping at grown-in defects was found in these samples.

1. Introduction

At the present time, positron annihilation, as a technique that can determine unambiguously the vacancy nature of a defect, is successfully applied to investigate the structure of intrinsic defects in III–V compound semiconductors (Dannefaer *et al* 1984, Dlubek and Krause 1987, Corbel *et al* 1988). However, it seems that positron annihilation has been scarcely applied to III–VI layered semiconductors. These compound semiconductors have a structure formed by layers containing four monatomic planes stacked in a sequence metalloid–metal–metal–metalloid. The bonding between atoms within a layer is covalent, while the inter-layer bonding is by van der Waals forces. As a result of this two-dimensional bonding scheme, the positron annihilation characteristics in these layered semiconductors could differ from those observed in typical III–V compound semiconductors.

Positron annihilation experiments have been performed on the layered semiconductor InSe in order to investigate the nature of the intrinsic defects responsible for its electrical and optical properties (de la Cruz *et al* 1988, 1989, 1992). These experiments have shown that certain lattice defects induced by electron irradiation can be effective positron traps. However, no evidence for positron trapping was found in as-grown and in heavily deformed InSe. Thermal equilibrium measurements in this compound semiconductor yield a temperature dependence of the positron annihilation parameters which could be attributed to thermal expansion of the lattice. Also, preliminary measurements performed on

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the layered semiconductor GaSe appeared to be consistent with a temperature dependence of the annihilation parameters governed by the lattice expansion (de la Cruz *et al* 1991).

It is crucial to know the temperature dependence of the positron annihilation parameters in the bulk, if the nature of the defects in III–VI compound semiconductors is going to be investigated by positron annihilation spectroscopy. The positron annihilation characteristics at low temperatures can give insight into the presence and nature of defects as effective positron traps in these materials.

Following McKee and McMullen (1978), the magnitude of the volume effect on the bulk positron lifetime is given by the volume coefficient

$$\gamma = (V/\tau)(\partial\tau/\partial V)_p = -(V/\lambda)(\partial\lambda/\partial V)_p \tag{1}$$

where $\tau = \lambda^{-1}$ is the bulk positron lifetime, V the volume and p the pressure. This volume coefficient can be obtained from the measured temperature coefficient of the positron lifetime χ by means of the relationship

$$\chi(T) = (1/\tau)(\partial\tau/\partial T)_p = -(1/\lambda)(\partial\lambda/\partial T)_p = \gamma\beta(T). \tag{2}$$

Here T is the temperature and $\beta(T) = V^{-1}(\partial V/\partial T)_p$ is the volume thermal expansion coefficient.

In metals, the temperature dependence of the bulk lifetime τ has been attributed to the combined effects of thermal lattice expansion and positron–phonon coupling (McKee and McMullen 1978, Stott and West 1978, Tam *et al* 1978). Therefore, it would be expected that the volume coefficient of τ is due to both thermal lattice expansion and vibration.

The present work reports the positron lifetime and Doppler broadening measurements performed on the layered semiconductors GaS, GaSe and GaTe at low temperatures. The observed temperature dependence of the annihilation parameters in GaS and GaSe is discussed in terms of their volume coefficients; the results reveal no evidence for positron trapping at the grown-in defects of these crystals.

2. Experimental details

The measurements were performed on single-crystal slabs of undoped GaS, GaSe and GaTe about 1.5 mm thick which were cleaved from large single crystals. The GaSe single crystals were grown by the Bridgman–Stockbarger method from material previously synthesized in a two-zone horizontal furnace. These crystals were p-type with a resistivity of about 10^3 Ω cm. The GaS and GaTe crystals were grown by the Bridgman technique. The GaS crystals had a semi-insulating behaviour. The GaTe samples had p-type conductivity with a resistivity of about 10 Ω cm. A ^{22}Na source with an activity of about 9×10^5 Bq deposited on a thin Ni foil was inserted into a single-crystal slab through a thin slot made by cleaving the slab carefully along a basal plane. Afterwards, the sample was slightly pressed to close the slot and fasten the source inside. The sample was set into a closed-He-cycle cryostat for positron lifetime and Doppler broadening measurements over the temperature range 8–320 K.

Positron lifetime measurements were performed using a fast coincidence system with a time resolution of 300 ps (FWHM). The lifetime spectra were analysed 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 spectrometer were determined from the lifetime spectrum analyses of several reference samples. A

Ge(Li) detector with a resolution of 1.35 keV at the 514 keV line of ^{85}Sr was used for the Doppler broadening measurements. These measurements were performed with the c axis of the samples parallel to the detector axis. The Doppler broadening of the annihilation peak is characterized by the lineshape parameters S and W, defined as the fraction of counts within an energy window ΔE of 2.10 keV centred at the peak, and of 1.8 keV between ±3.3 and ±5.1 keV, respectively.

3. Results

The positron lifetime spectra for all the samples are of a single-component nature in the temperature range 8–320 K. The positron lifetime versus temperature for as-grown GaS, GaSe and GaTe is shown in figure 1. The observed trend of the positron lifetime is to increase with increasing temperature except in GaTe, where it increases from 307 to 313 ps in the temperature range 20–50 K and stays constant at $\tau = 313 \pm 2$ ps, for $T \geqslant 50$ K. The temperature dependence of τ, obtained by integration of equation (2), would be

$$\tau = \tau_0 \exp\left(\int_{T_0}^{T} \gamma\beta(T)\,\mathrm{d}T\right) \simeq \tau_0\left(1 + \gamma\int_{T_0}^{T} \beta(T)\,\mathrm{d}T\right) \tag{3}$$

where γ is the volume coefficient of τ, assumed constant, T_0 the lower temperature of the experimental points, τ_0 the positron lifetime at T_0, and $\beta(T)$ the volume expansion coefficient.

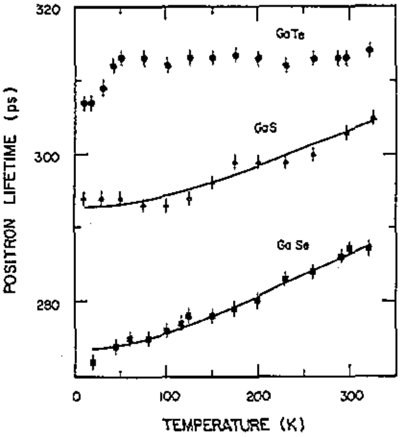

Figure 1. Positron lifetime for as-grown GaS, GaSe and GaTe as functions of temperature. The curves represent the fit of the data to equation (3).

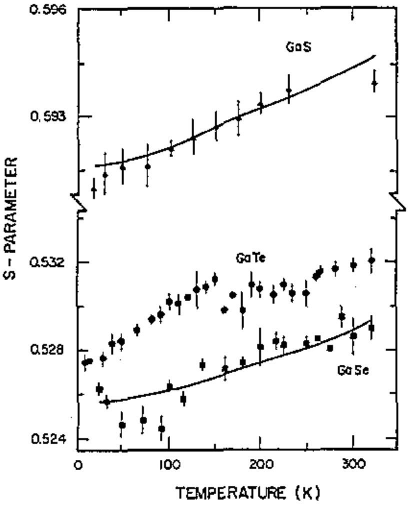

Figure 2. The parameters S for as-grown GaS, GaSe and GaTe as functions of temperature. The curves represent the fit of the data to equation (4).

The values of the parameters S and W in as-grown GaS, GaSe and GaTe as functions of temperature are shown in figures 2 and 3, respectively. In the same way as above, the observed temperature dependence of these parameters could be described by

$$S = S_0 \exp\left(\int_{T_0}^{T} \delta\beta(T)\,\mathrm{d}T\right) \simeq S_0\left(1 + \delta\int_{T_0}^{T} \beta(T)\,\mathrm{d}T\right) \tag{4}$$

and

$$W = W_0 \exp\left(\int_{T_0}^{T} \epsilon\beta(T)\,\mathrm{d}T\right) \simeq W_0\left(1 + \epsilon\int_{T_0}^{T} \beta(T)\,\mathrm{d}T\right) \tag{5}$$

where δ and ϵ are the volume coefficients of S and W, respectively, assumed constant in the range of temperatures investigated and defined in the same way as γ in equation (1).

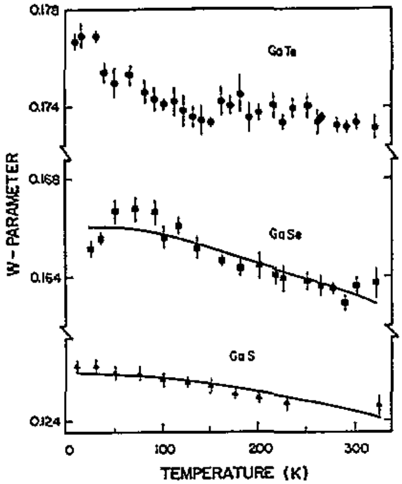

Figure 3. The parameters W for as-grown GaS, GaSe and GaTe as functions of temperature. The curves represent the fit of the data to equation (5).

The experimental points in figures 1, 2 and 3 can be fitted to equations (3), (4) and (5), respectively, by a least-squares method. For GaS and GaSe, the volume expansion coefficient $\beta(T) = 2\alpha_{\parallel}(T) + \alpha_{\perp}(T)$ is obtained from the experimental values of $\alpha_{\parallel}(T)$ and $\alpha_{\perp}(T)$ reported by Belenkii *et al* (1982, 1984, 1985); $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the linear expansion coefficients in the basal plane and along the c axis, respectively. The temperature dependences of $\alpha_{\parallel}$ and $\alpha_{\perp}$ are found to be properly described by third-degree polynomials in GaS and GaSe for temperatures below the Debye temperature T_{D}, i.e. 300 K in GaS and 200 K in GaSe (Belenkii *et al* 1984). For temperatures $T \geqslant T_{\mathrm{D}}$, the thermal expansion coefficients are assumed to be constant. The adjustments result in the following values: $\tau_0 = 293.2$ ps, $\gamma = 7.5$, $S_0 = 0.5917$, $\delta = 0.9$, $W_0 = 0.1260$ and $\epsilon = -2.8$ for GaS, $\tau_0 = 274.0$ ps, $\gamma = 9.0$, $S_0 = 0.5255$, $\delta = 1.4$, $W_0 = 0.1660$ and $\epsilon = -3.4$ for GaSe.

The temperature dependence of the annihilation parameters in GaTe cannot be analysed in similar terms because experimental data on its thermal expansion coefficients have not been found in the literature.

4. Discussion

The total failure of the two-component analyses of the lifetime spectra, together with the observed temperature dependence of the annihilation parameters in GaS and GaSe, can be interpreted as a clear sign of the absence of positron trapping in these samples because of the following. In the case of negatively charged positron traps, an increase in the low-temperature trapping in semiconductors is expected for decreasing temperature because of the temperature dependence of their trapping coefficient (Puska *et al* 1990). However, the measured annihilation parameters do not show a positron-trapping increase for decreasing temperature, with the exception of the parameters S and W in GaSe for temperatures below about 90 K; this point will be discussed later. Thus, negatively charged defects can be ruled out as the defects responsible for plausible low-temperature trapping. On the other hand, if the positron traps were neutral, their trapping coefficients would be temperature independent (Puska *et al* 1990). This means that if there were neutral positron traps in these samples, the observed temperature dependence of the annihilation parameters can be attributed to a change in the trap concentration, and/or to an increase in the trapping coefficient, induced by a change in the charge state of the traps. This could be produced by a shift in the Fermi level position in the gap. For p-type semiconductors, the Fermi level moves upwards with increasing temperature, so that acceptor vacancy-type centres could be ionized, becoming effective positron traps if their energy level is crossed by the Fermi level. However, the absolute impossibility of separating out a second lifetime component in the spectra and the fairly good fit of the experimental data for GaS and GaSe to a temperature dependence controlled by the thermal effects on the lattice support the absence of positron trapping in these samples.

In GaSe, the observed increase in S, or the decrease in W, for decreasing temperatures below about 90 K seems not to be actually due to positron trapping because it is not accompanied by an increase in τ. It should be mentioned that the linear expansion coefficient $\alpha_{\|}$ of GaSe becomes negative in the temperature interval $30\ \mathrm{K} \leqslant T < 60\ \mathrm{K}$ (Belenkii *et al* 1982, 1984, 1985). We cannot account for the discrepancy between the temperature dependences of τ and S, or τ and W, in GaSe but suggest that it may be a combined effect of the strong anisotropy of the crystal, the unidirectional character of the measured parameters S and W and the negative value of $\alpha_{\|}$.

In GaTe, the absence of positron trapping cannot be convincingly maintained. The temperature dependence of the annihilation parameters could be attributed to an increase in the positron trapping induced by a Fermi-level-controlled change in the charge state of vacancy-type acceptor centres taking place for T above about 30 K.

The γ-values found reveal a noticeable volume effect on the bulk lifetime of GaS and GaSe. On the contrary, the values obtained for the volume coefficient of S, i.e. the δ-values, are around unity, suggesting a smaller contribution to the temperature dependence of S. An estimation of the volume effect on the partial positron annihilation rate with core electrons is given by its volume coefficient γ_c obtained from equation (A3) in the appendix. Values of $\gamma_c = 10.3$ for GaS, and $\gamma_c = 12.4$ for GaSe, are obtained. The fact that the $|\epsilon|$-values are significantly higher than the δ-values also indicates that the volume effect on the annihilation process with core electrons is stronger than that with valence electrons.

5. Conclusions

The observed temperature dependence of the annihilation parameters in the III–VI layered semiconductor GaS and GaSe reveals an important volume effect on the positron annihilation process with core electrons.

The temperature dependence of the positron lifetime in GaS and GaSe are consistent with the absence of positron trapping in grown-in defects. Values of 293 ps and 274 ps, respectively, are proposed for the bulk positron lifetime in GaS and GaSe at about 10 K.

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Appendix

The contribution of low-momentum e^-–e^+ pairs to the value of W is usually very low so that it is reasonable to assume that $W \propto \lambda_c/\lambda$, where $\lambda = \tau^{-1} = \lambda_v + \lambda_c$ is the total annihilation rate, and λ_v and λ_c are the annihilation rates with valence and core electrons, respectively; the separation of λ into partial annihilation rates is assumed to be valid for GaS and GaSe according to the models for positrons in GaAs (Puska *et al* 1986, Puska and Corbel 1988). Then, it is easy to see that

$$\begin{aligned}(\partial \ln W/\partial T)_p &= (1/\lambda_c)(\partial\lambda_c/\partial T)_p - (1/\lambda)(\partial\lambda/\partial T)_p \\ &= \chi(T) - \chi_c(T) \end{aligned} \tag{A1}$$

where $\chi_c(T) = -(1/\lambda_c)(\partial\lambda_c/\partial T)_p$ can be expressed as

$$\chi_c(T) = \gamma_c\beta(T). \tag{A2}$$

Here the volume coefficient $\gamma_c = -(V/\lambda_c)(\partial\lambda_c/\partial V)_p$ is also assumed constant.

From equations (5), (A1) and (A2), we obtain

$$\epsilon = \gamma - \gamma_c. \tag{A3}$$

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