RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 48, NUMBER 12 15 SEPTEMBER 1993-II

Positron binding energies and specific trapping rates for monovacancies in GaAs and InSb

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(Received 1 April 1993)

Positron measurements on as-grown GaAs and InSb in the temperature range 30–800 K have resulted in an experimental determination of the positron binding energies and absolute specific trapping rate for monovacancies. In the case of GaAs the binding energy is found to be 0.30±0.02 eV and the absolute specific trapping rate to be $(1.0\pm0.2)\times10^{-17}$ $ns^{-1}\,cm^3$. In the case of InSb the binding energy is constant (0.28±0.02 eV) below ~540 K but increases to 0.60±0.05 eV close to the melting point (823 K).

In order to determine experimentally the positron binding energy for a particular defect type it is necessary to observe detrapping from the defect. This has been done for different types of defects exhibiting detrapping at low temperatures (≈150 K).[1] These defects (shallow traps) are of such a nature that they represent little or no open volume for the positrons. The binding energies are small and in the 20–60-meV range.

Only a few positron investigations on GaAs at elevated temperatures have been published (and none that we are aware of on InSb). Saarinen, Hautojärvi, and Lanki[2] investigated *n*-type GaAs up to 600 K using lifetime spectroscopy, interpreting their results in terms of Fermi-level-controlled charge states of arsenic vacancies. Soininen *et al.*[3] investigated positron diffusion (using positron beam and doppler broadening techniques) in *n*-type GaAs up to 800 K.

In this work we present an experimental determination of the positron binding energy for monovacancies, i.e., for a defect type with a substantial open volume. These measurements have also made possible a direct experimental determination of the absolute specific trapping rate, thus avoiding the usual calibration procedure with nonpositron data.

Two types of samples were investigated, undoped semi-insulating GaAs and undoped InSb, both in their as-grown state. Positron lifetime measurements were done using a spectrometer with a time resolution of 250 ps (full width at half maximum) and each spectrum contained $\sim6\times10^6$ counts accumulated over a period of ~18 h. The positron source (10 μCi ^{22}NaCl) was encapsulated in two layers of Al foils, each of thickness 1 μm.

Since the measurements were conducted up to 800 K of sample temperature (as measured with a Pt/Pt-Rh thermocouple in close proximity to the samples), special care was taken to correct for the temperature-dependent source correction to which there were two contributions. The first arises from the source itself, amounting initially to 250 ps with an intensity of 4% (characteristic for heavily deformed Al). The sample-source assembly was heated in one step to 800 K which anneals the aluminum foil, but also generates thermal vacancies in the foil. We have used the data as obtained by Hall, Goland, and Snead[4] to create the temperature-dependent Al source correction which varies between ~165 ps below ~450 K and 238 ps above ~600 K. The second source contribution arises from the oven. During the first high-temperature measurement on InSb the samples reacted with a copper part of the sample holder resulting in the source being exposed and the oven becoming slightly contaminated. The holder was modified and the oven cleaned but a small contribution from the oven remained. This component was measured independently (i.e., without the sample-source assembly) up to 800 K and amounted to only 1%. Since NaCl may migrate at the high temperatures involved, the oven component was measured repeatedly and was found to remain constant at 1%. In addition, the results for both samples were found to be reproducible for three temperature cycles between 300 and 800 K. In Table I are shown the effects of these source corrections for a spectrum obtained at 569 K, where these corrections are of particular importance.

Before the high-temperature measurements, heat treatments of similar samples were done up to 800 K in steps of 100 K. No effect from this treatment was evident as measured at room temperature for either GaAs or InSb.

In Fig. 1 are shown data for the GaAs sample after the source corrections. Two lifetimes (plus a weak 0.3% 1.3-ns lifetime) could be resolved with the longer lifetime $\tau_2\simeq270$ ps (in the 30–400-K temperature range) attributed as usual to positrons trapped in monovacancies.

In a sample where no positron trapping takes place, positrons annihilate with the bulk lifetime τ_B, which is dependent on the material and for GaAs has the value 220 ps.[5] τ_B should show only a small temperature dependence reflecting lattice expansion. When trapping does occur, then according to the simple trapping model[6] a calculated bulk lifetime may be obtained according to

$$(\tau_B^{\mathrm{TM}})^{-1}=I_1(\tau_1^{-1})+I_2(\tau_2^{-1}) \;, \tag{1}$$

where $I_1+I_2=1$.

It is straightforward to show that this expression is also valid when detrapping (discussed below) occurs. As seen in Fig. 1, τ_B^{TM} exhibits the expected behavior indicating the applicability of the trapping model employed.

To explain the temperature variations of τ_1, τ_2, and I_2 we consider the possibility that detrapping occurs from the monovacancies grown into the sample. According to Pagh *et al.*,[7] the values of these parameters are given by

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TABLE I. Influence from different source corrections on the final results. The sample is GaAs at 569 K.

Source correction	τ_1 (ps)	τ_2 (ps)	τ_3 (ns)	I_1 (%)	I_2 (%)	I_3 (%)
None	172±6	254±5	1.1±0.1	29±2	71±4	0.30±0.05
Al foil only[a]	182	257	1.1	35	65	0.30
Al foil + oven[b]	182	258	1.1	35	65	0.30

[a]106 ps, 1.4%; 238 ps, 2.6%.
[b]106 ps, 1.4%; 240 ps, 3.6%.

$$\tau_1^{-1} \equiv \lambda_1 = (\lambda_B + \lambda_T + \kappa + \delta + d)/2 \ , \tag{2}$$

where λ_B is the bulk annihilation rate and λ_T is the annihilation rate of positrons trapped with rate κ and detrapped with δ. The quantity d is

$$d = [(\lambda_B - \lambda_T + \kappa - \delta)^2 + 4\kappa\delta]^{1/2} \ . \tag{3}$$

The second lifetime is given by

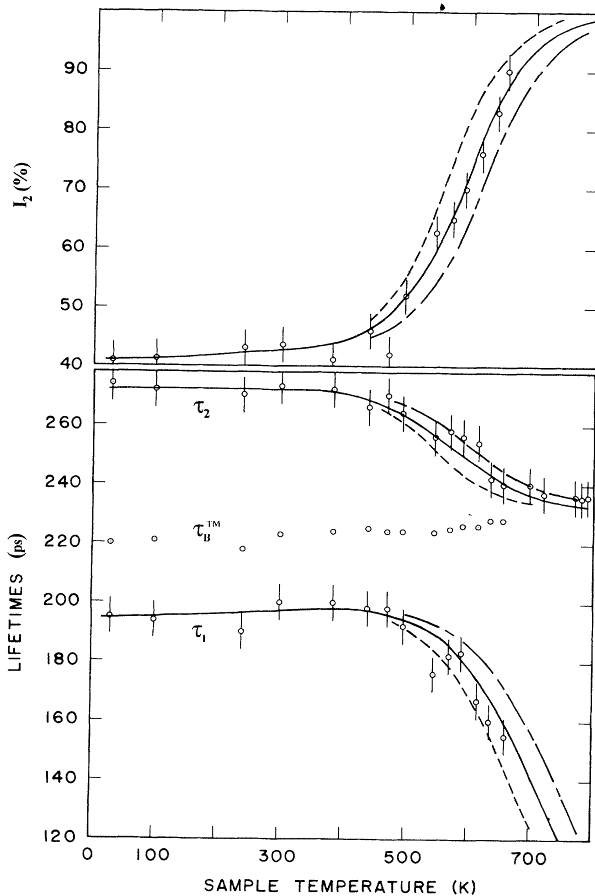

FIG. 1. Positron lifetime data for sample temperatures of 30–790 K for undoped semi-insulating GaAs. The solid lines represent the best fit for a positron binding energy of $E_B = 0.30$ eV and an absolute specific trapping rate of 0.9×10^{-17} cm^3/ns. The broken curves (— — —) are for $E_B = 0.28$ eV and the (—-—-) curves are for $E_B = 0.32$ eV, illustrating the strong sensitivity of the fits to the chosen value of E_B. Above 700 K it was possible experimentally to resolve only one lifetime component, so no τ_B^{TM} values can be calculated.

$$\tau_2^{-1} \equiv \lambda_2 = \lambda_1 - d \ . \tag{4}$$

Finally, the intensity $I_2(=1-I_1)$ of the τ_2 component is

$$I_2 = [\lambda_T \kappa + (\lambda_T + \delta - \lambda_2)\lambda_B]/d\lambda_2 \ . \tag{5}$$

According to Manninen and Nieminen,[8] the detrapping rate δ from a single trap type is given by

$$\delta = \mu(mk_BT/2\pi\hbar^2)^{3/2} e^{-E_B/k_BT} \ , \tag{6}$$

where μ denotes the trapping rate per unit absolute defect concentration, i.e., the absolute specific trapping rate (in convenient units of cm^3/ns), and m the effective mass for the positron ($\simeq m_0$) and E_B the positron binding energy. It is noteworthy that when no detrapping occurs ($\delta = 0$) it is *not* possible to obtain a value for μ, but that this is possible when $\delta > 0$.

For a detrapping rate of zero, τ_2^{-1} equals λ_T, i.e., the annihilation rate for the trapped positrons, and the trapping rate is given by

$$\kappa = I_2[(\tau_B^{TM})^{-1} - (\tau_2)^{-1}]/(1 - I_2) \ . \tag{7}$$

When the detrapping rate $\delta \to \infty$, $\tau_1 \to 0$, $\tau_2 \to \tau_B$, and $I_2 \to 100\%$, corresponding physically to the situation that no annihilations from the trap can be observed. We thus see that the *physical* meaning of the lifetime components changes radically with the detrapping rate. The data shown in Fig. 1 exhibit exactly these trends. At low temperatures the constancy of τ_1, τ_2, and I_2 shows that $\delta = 0$ and using Eq. (7) we find a value of $\kappa = 0.6$ ns^{-1} as we commonly have found for as-grown GaAs regardless of conductivity type.

At higher temperatures the data were fitted assuming different E_B *and* μ values, but κ was kept constant at 0.6 ns^{-1}. The fits are very sensitive to the value of E_B and the best fits (minimum χ^2) are obtained for E_B values in the range of only 0.30±0.02 eV with corresponding values of μ between 0.9 and 1.3×10^{-17} cm^3/ns. The fact that the three experimentally determined parameters (τ_1, τ_2, and I_2) can be fitted over a range of 30–790 K by only two adjustable parameters (E_B and μ) is quite convincing evidence for the applicability of the model employed. Nevertheless, because of a concern that the high-temperature results might be due to a systematic artifact, it is noted that no such effects were observed in the case of silicon or diamond[9] samples. The annihilation parameters in these cases were essentially constant over the entire temperature range.

The data obtained for InSb, in the same fashion as

those for GaAs, are shown in Fig. 2. The data have the same trend as in the case for GaAs up to ~ 540 K, but display above this temperature a reversal in trends as the melting temperature (823 K) is approached. The calculated bulk lifetime [from Eq. (1)] is nearly constant, around 263 ps, increasing only slightly at higher temperature.

The positron lifetime of 308 ps indicates again a monovacancy response though it is not clear (*a priori*) if it arises from V_{In} or V_{Sb} or both. Theoretical calculations[10] suggest that the increase in lifetime from the bulk lifetime is 35 ps for V_{In} and 42 ps for V_{Sb}, placing the experimentally obtained value of 44 ps close to V_{Sb}. The theoretical bulk lifetime of 280 ps deviates somewhat from the experimental $T=0$ K value of 263 ps. The data could again be fitted with the model laid out in Eqs. (2)–(6) but in order to obtain the reversal in trends above ~ 540 K, it was necessary to increase E_B as a function of temperature. An added complication is that vacancies may be thermally generated close to the melting point, i.e., the trapping rate may not necessarily be constant and, finally, the absolute specific trapping rate may also change close to the melting point. Extensive calculations were done varying the above-mentioned fitting parameters (E_B, κ, and μ), but it was found, as expected, that the decisive parameter was E_B. In Fig. 3 is shown the temperature variation for E_B. Variations of κ in the range $0.9-1.5$ ns^{-1} and absolute specific trapping rates in the range $(0.5-2.0)\times 10^{-17}$ cm^3/ns were not detrimental to the fits. Although a global fitting procedure was not attempted, it can be stated that it was not possible to obtain a satisfactory fit in the whole temperature range with a single value of E_B for any combination of μ and κ. Choosing $\mu=1.1\times 10^{-17}$ cm^3/ns (obtained by multiplying the GaAs μ value by the ratio between the atomic density of GaAs and InSb) and $\kappa=1.1$ ns^{-1} (to agree with the low-temperature data for InSb), theoretical curves for τ_1, τ_2, and I_2 are shown in Fig. 2 using interpolated E_B values from Fig. 3.

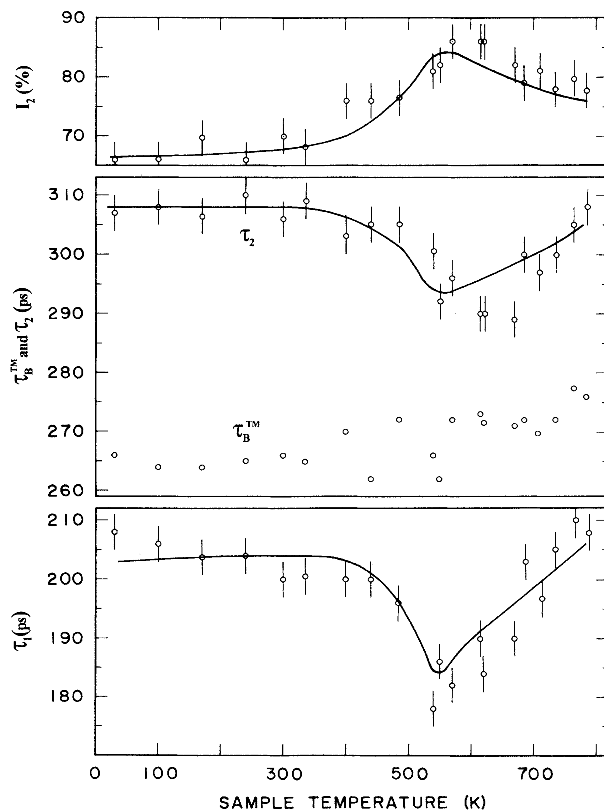

FIG. 2. Positron lifetime data for undoped InSb. The solid lines represent a fit using a variable binding energy (according to Fig. 3) obtained by best fitting at various temperatures. The absolute specific trapping rate and the trapping rate were kept constant at 1.1×10^{-17} cm^3/ns and 1.1 ns^{-1}, respectively.

We conclude, therefore, that the positron binding energy increases significantly, beginning about 300 K below the melting point, and reaches a value near the melting point such that hardly any detrapping occurs. The dependence of the positron-vacancy binding energy on temperature has been examined theoretically by Manninen and Nieminen[8] who show that there are two opposing effects. Thermal expansion of the lattice decreases the binding energy while lattice vibrations increase the binding energy and, further, lattice vibrations have the potential to play a dominant role resulting in strongly increased binding energy. The present experiments support this theoretical prediction.

The fitting procedure described above showed that the vacancy concentration at 800 K (23 K below the melting point) could at most be ~ 3 times the concentration of vacancies retained after the growth. This suggests that the vacancies are bound by impurities (or antisites) with a binding energy sizable compared to the vacancy formation energy.

The positron binding energy obtained in this work for GaAs of 0.30 eV is close to the theoretical value[10] for V_{As} (0.24 eV) and deviates significantly from the theoretical value for V_{Ga} of 0.44 eV. We note that the theoretical

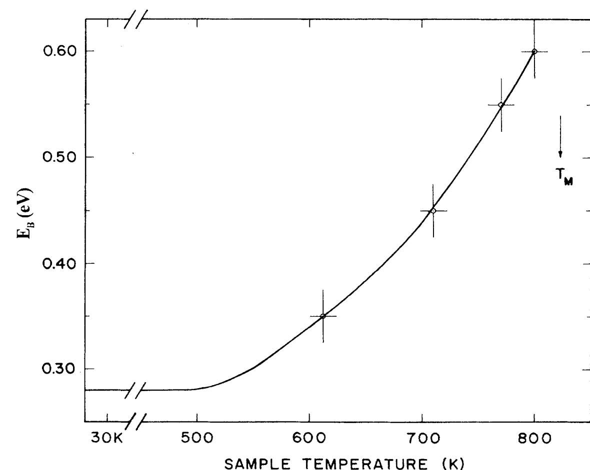

FIG. 3. Variation of binding energy E_B for InSb as suggested by best fitting of the data in Fig. 2 below 500 K, at 610, 710, 770, and 800 K. Reasonable fits could be obtained for absolute specific trapping rates in the $(0.5-2.0)\times 10^{-17}$-cm^3/ns range and trapping rates in the $0.9-1.5$-ns^{-1} range.

values for the position lifetimes trapped in V_{As} or V_{Ga} are too close (265 versus 268 ps, respectively) to be experimentally resolvable, but a distinction seems to be possible by virtue of the binding energies. For InSb the theoretical binding energies are 0.30 and 0.26 eV for V_{In} and V_{Sb}, respectively, too close to be distinguishable experimentally given the uncertainty in the absolute specific trapping rate, but on the other hand the V_{Sb} lifetime increase (of 42 ps) is close to the experimental value. Thus in GaAs the data indicate trapping by V_{As} and in InSb by V_{Sb}, and in view of their thermal stability (at least up to 800 K) these vacancies are probably trapped by impurities or other structural defects with overall neutral charge as argued earlier in the case of GaAs.[5] For both samples we have found that the assumption of detrapping from a single trap type with temperature-independent trapping rate (implying that the defects do not change their charge state with temperature) explains well the observed temperature dependencies of the positron parameters.

In conclusion, we have determined experimentally the positron binding energy as well as the absolute specific trapping rate for monovacancies in GaAs and InSb. Binding energies support values obtained by theoretical calculations, and absolute specific trapping rates agree quite well with former estimates derived from comparisons with nonpositron data,[11] as well as with theoretical estimates for neutral vacancies.[12] This work has also demonstrated that conventional positron lifetime measurements can successfully be made at least up to 800 K.

We are indebted to Professor P. Mascher (McMaster University, Hamilton, Canada) for performing the initial measurements and to Dr. T. Bretagnon (Université de Montpellier, Montpellier, France) for implementing the detrapping model on the computer. This research was supported by the Natural Sciences and Engineering Research Council of Canada.

[1]C. Corbel, F. Pierre, K. Saarinen, and P. Hautojärvi, Phys. Rev. B **45**, 3386 (1992).

[2]K. Saarinen, P. Hautojärvi, and P. Lanki, Phys. Rev. B **44**, 10 585 (1991).

[3]E. Soininen, J. Mäkinen, D. Beyer, and P. Hautojärvi, Phys. Rev. B **46** 13 104 (1992).

[4]T. M. Hall, A. N. Goland, and C. L. Snead, Jr., Phys. Rev. B **10**, 3062 (1974).

[5]D. Dannefaer, P. Mascher, and D. Kerr, J. Phys. Condens. Matter **1**, 3213 (1989).

[6]R. N. West, in *Positrons in Solids,* edited by P. Hautojärvi, Topics in Current Physics Vol. 12 (Springer-Verlag, Berlin, 1979).

[7]B. Pagh, H. E. Hansen, B. Nielsen, G. Trumpy, and K. Petersen, Appl. Phys. A **33**, 255 (1984).

[8]M. Manninen and R. M. Nieminen, Appl. Phys. A **26**, 93 (1981).

[9]S. Dannefaer, P. Mascher, and D. Kerr, Diamond Relat. Mater. **1**, 407 (1992).

[10]M. J. Puska, S. Mäkinen, M. Manninen, and R. M. Nieminen, Phys. Rev. B **39**, 7666 (1989).

[11]P. Mascher, S. Dannefaer, and D. Kerr, Phys. Rev. B **40**, 11 764 (1989).

[12]M. J. Puska, C. Corbel, and R. M. Nieminen, Phys. Rev. B **41**, 9980 (1990).