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Positron line-shape parameters and lifetimes for semiconductors: Systematics and temperature effects

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Positron Doppler broadening and lifetime experiments have been performed on C (diamond), SiC, Si, Ge, GaN, GaP, GaAs, GaSb, InP, InAs, and InSb. It was found that the Doppler-broadening parameter arising from valence electrons depends linearly on the free-electron gas r_s value when calculated from the valence-electron density. Positron lifetimes due to valence electrons are found to be proportional to r_s^3. Finer details, which result from the bonded character of the valence electrons, are revealed by slight anisotropies of the S parameter. Temperature dependencies in the 100–600-K temperature range studied by means of Doppler broadening show a complex behavior which in part may be defect influenced. [S0163-1829(96)01448-8]

I. INTRODUCTION

In the original theoretical work by Brandt and Reinheimer,[1] it was suggested that the annihilation rate of positrons in semiconductors could be assessed by assuming the valence electrons to be a free-electron gas. The presence of a band gap resulted in a slightly reduced enhancement factor compared to a truly free-electron gas. Experimental work[2] later confirmed the applicability of this model. More recent calculations by Puska *et al.*[3] included the contribution arising from core electrons to the total annihilation rate, which makes possible a further investigation of positron annihilation in semiconductors by separating valence and core contributions to both Doppler and lifetime data.

In this paper we report on Doppler-broadening experiments and further lifetime experiments with the primary purpose of investigating if *general* features of the valence-electron momentum distribution can also be explained by the model suggested by Brandt and Reinheimer.[1] We find this to be the case provided contributions from core-electron annihilations are taken into account. In addition, the Doppler parameter was investigated in the 100–600-K range with the purpose of elucidating temperature effects.

II. EXPERIMENT

Lifetime measurements were made using standard spectrometers with a time resolution of 180–200 ps, and analyses were based on the RESOLUTION program.[4] Doppler measurements were obtained using a Ge detector with an energy resolution of 1.2 keV at 0.511 MeV. The bell-shaped Doppler spectra were analyzed (after background subtraction) in terms of the S parameter as defined by the number of counts within the centered 511±0.7-keV range divided by the number of counts in the 511±4.8-keV range. Although this parameter is dominated by the low-momentum valence electrons, it also contains a contribution from high-momentum core electrons. Another parameter W was also calculated. For this parameter the number of counts situated in the wings of the energy spectrum was divided by the number of counts in the 511±4.8-keV range. The two wing energy ranges, each of width 1.6 keV, were centered at 511±3.3 keV. Although the W parameter is more strongly influenced by core-electron momenta in comparison to the S parameter, W is also influenced by valence electrons. Generally, an increase in S is expected to result in a decrease in W, although we will demonstrate absence of a simple relationship between S and W.

III. RESULTS AND DISCUSSION

Table I lists experimentally obtained values of S_{expt} and W_{expt}. In order to define a material-related parameter on which S_{expt} could depend, we take recourse to the free-electron model for the valence electrons.[1] One can then define an r_s parameter from

$$\frac{4\pi}{3} r_s^3 = n_{\mathrm{val}}^{-1}, \tag{1}$$

where n_{val} is the density of valence electrons as based on all available volume. It could be argued that in calculating r_s one should exclude the ion core volume, but such a correction amounts to less than 2%, for which reason it has been omitted. r_s is then inversely proportional to the ''Fermi'' momentum p_F, and using this momentum as characteristic of the momentum spread, to which S_{expt} would be inversely proportional, one might expect S_{expt} to be proportional to r_s. (We have verified by computer simulations that S values obtained by folding various parabolic momentum distributions of free electrons with the Gaussian detector response function are indeed inversely proportional to p_F.)

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TABLE I. Experimental results for S_{expt} and W_{expt} (obtained at room temperature) ordered according to increasing r_s values, i.e., with decreasing valence-electron density. S_{val} is the calculated S parameter for valence electrons using the core fractions f_c from Puska *et al.*'s data (Ref. 3). The second-last column lists the ratio between the ''Fermi'' momentum for the valence electrons and the momentum for the outermost core electrons. The last column summarizes the nature of the investigated samples. *Uncertainties in W_{expt} and S_{expt} large due to the large backing contribution. †Average values for S- or Zn-doped GaP (S_{expt}=0.4806 and 0.4925, respectively, and W_{expt}=0.0397 and 0.0372, respectively). ††Average values. 1 Ω cm: S_{expt}=0.5013, W_{expt}=0.0375; 50 Ω cm: S_{expt}=0.5023, W_{expt}=0.0373.

Material	Band gap (eV)	r_s (Å)	f_c (%)	W_{expt} ±0.0003	S_{expt} ±0.0005	S_{val}	p_F/p_n^{core}	Comments
C	5.5	0.70	1.20	0.0660	0.4071	0.4099	0.43	synthetic, type I_b
SiC	3.0	0.85	2.65	0.0450	0.4376	0.4441	0.44	n type, N doped
GaN	3.4	0.88	14.0	0.053±0.003*	0.455 ±0.005*	0.4913	0.43	12-μm-thick film on sapphire
Si	1.1	1.06	2.25	0.0230	0.5098	0.5158	0.41	Fz-Si, undoped
GaP	2.2	1.07	6.87	0.0385†	0.4865†	0.5057	0.38	p type, n type
Ge	0.7	1.11	6.80	0.0374††	0.5018††	0.5261	0.32	n type: 1 Ω cm and 50 Ω cm
GaAs	1.4	1.11	7.80	0.0385	0.4970	0.5230	0.33	semi-insulating
InP	1.3	1.15	8.33	0.0357	0.5034	0.5298	0.37	semi-insulating
InAs	0.36	1.18	8.79	0.0377	0.5132	0.5435	0.33	n type, undoped
GaSb	0.67	1.19	7.38	0.0345	0.5183	0.5451	0.30	n type, Te doped
InSb	0.17	1.27	7.92	0.0346	0.5277	0.5567	0.30	n type, undoped

Plotting S_{expt} versus r_s [see Fig. 1(a)] does seem to indicate a straight-line relationship, except for the Si data point whose value appears to be too large. The reason for this is not related to vacancies (which should increase S_{expt}) because the lifetime data in Table II indicate no such contribution. It is not easy to dismiss the Si data point as an ''aberration,'' and indeed it is not, as will be seen below.

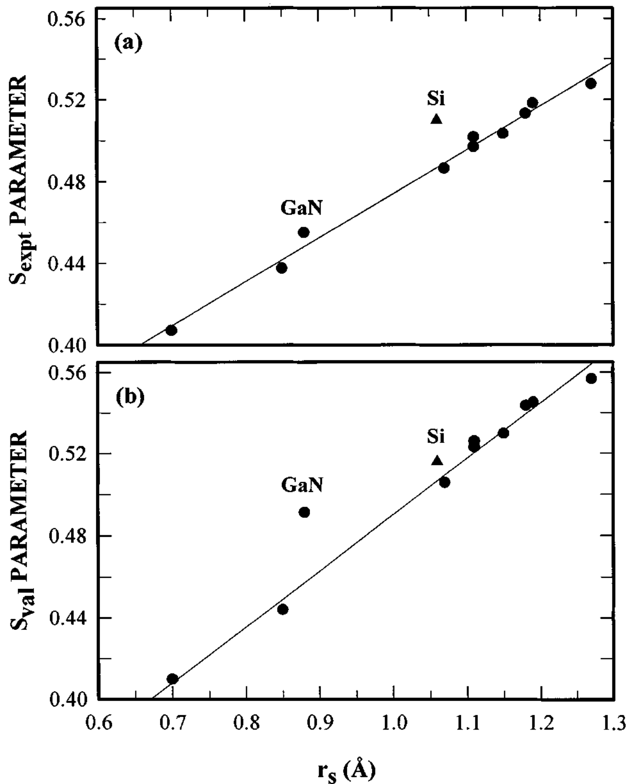

FIG. 1. (a) Experimentally obtained S_{expt} values as a function of r_s. All measurements were made at room temperature. (b) Calculated S_{val} values for valence electrons. The large value for GaN arises because of an uncharacteristically large calculated core contribution.

The experimentally measured S values contain, in the absence of defects, *two* contributions, one from valence electrons and one from core electrons, so that

$$S_{expt}=(1-f_c)S_{val}+f_cS_c, \tag{2}$$

where f_c is the fraction of positrons annihilating with core electrons, S_c their characteristic Doppler parameter, and S_{val} is that for the valence electrons: Clearly, S_{val} rather than S_{expt} should be correlated with r_s.

In order to obtain values for S_{val}, we proceed as follows: The fraction of positrons annihilating with core electrons is given by

$$f_c=\lambda_c/(\lambda_c+\lambda_{val}). \tag{3}$$

λ_c is the annihilation rate of positrons with core electrons and, λ_{val} that for valence electrons; the sum $(\lambda_c+\lambda_{val})$ is the inverse of the experimentally determined bulk lifetime τ_B. Puska *et al.*[3] calculated theoretical values of λ_c, from which we have determined f_c values (see Table I) using our bulk lifetimes listed in Table II. Theoretical calculations of either S_{val} or S_c are presently unavailable, so we estimate the ratio S_c/S_{val} according to the following simple arguments: Assuming only the outer core electrons to contribute to S_c, S_c would be inversely proportional to $p_n^{core}=n\hbar/r_{ion}$, where n is the main quantum number of the outer core electrons, and r_{ion} the ionic radius. Likewise, S_{val} would be inversely proportional to the ''Fermi'' momentum p_F, so that S_c/S_{val} can be approximated by p_F/p_n^{core}, where p_F equals $2\hbar/r_s$ according to the free-electron theory. p_n^{core} was calculated using r_{ion} values from Ref. 5, and in the cases of compound semiconductors the average of p_n^{core} arising from each element was calculated. Results of p_F/p_n^{core} are listed in Table I. Our rough estimates of 0.3–0.4 compare well with the more de-

TABLE II. Lifetime data for 11 semiconductors ordered according to decreasing valence-electron density. All measurements were done at room temperature. The bulk lifetime τ_B is calculated from the trapping model (Ref. 15) according to $1/\tau_B=(1-I_2)/\tau_1+I_2/\tau_2$. The trapping rate is calculated from $\kappa=1/\tau_1-1/\tau_B$ and the trapped fraction is $f_T=\kappa/(\kappa+1/\tau_B)$. τ_{val} is the lifetime arising from annihilation with valence electrons only. The last column summarizes the nature of the investigated samples.

Material	τ_1 (ps)	τ_2 (ps)	I_2 (%)	τ_B (ps)	κ (ns^{-1})	f_T (%)	τ_{val} (ps)	Comments
C	105	430	3	107± 1	~0	~0	109	synthetic, type I_b
SiC	140	343	3	144± 2	~0	~0	148	p type, n type
GaN	126	259	50	170±10	2.1	26	198	12-μm-thick film on sapphire
Si	218		0	218± 1	0	0	223	Fz-Si, undoped
GaP	193	272	42	220± 4	0.6	12	236	p type, n type
Ge	178	250	60	219± 4	1.0	18	235	50 Ω cm n type
Ge	196	290	33	222± 4	0.6	12	238	1 Ω cm n type
GaAs	190	265	45	219± 2	0.7	13	237	n type, semi-insulating
InP	190	267	67	236± 2	1.0	20	256	n type, p type, semi-insulating
InAs	202	288	60	246± 4	0.9	18	269	n type, undoped
GaSb	194	297	67	253± 4	1.2	23	273	n type, Te doped
InSb	200	305	70	265± 3	1.2	25	287	n type, p type

tailed calculations (for Al) by Lynn *et al.*[6] From their Fig. 2 it can be inferred that the full width at half maximum of the valence electron momentum distribution is approximately 1/3 of that for the $2p^6$ electrons.

Since the value of f_c is at most 0.09 (omitting the uncharacteristically large value of 0.14 for GaN) one finds from Eq. (2), to the first order in f_c,

$$S_{val}=S_{expt}\left[1+f_c\left(1-\frac{S_c}{S_{expt}}\right)\right]. \quad (4)$$

Using for S_c/S_{expt} the estimated values of S_c/S_{val} $(=p_F/p_n^{core})$, we obtain values of S_{val} as listed in Table I, and these are plotted in Fig. 1(b).

The correction for core contributions places the data on a straight line (except for GaN, as caused by the questionably large theoretical value of f_c). This simple relation may be somewhat fortuitous for two reasons: First, our estimate for S_c is crude, and, second, the lifetime data in Table II indicate that many of the samples contain grown-in vacancies which would increase S_{expt}, so to yield erroneously large values of S_{val}. However, the increase in S_{expt} would be small (<1%). This is based on the estimate that the S parameter for vacancies is about 4% higher than for the bulk,[7] so that with a trapped fraction of at most $\frac{1}{4}$ (f_T in Table II), this would predict an increase of less than 1%.

We conclude, therefore, that after correction for the core contribution to S_{expt} there is a linear relation between S_{val} and r_s, an observation which further substantiates the theoretical models of Brandt and Reinheimer[1] and Puska *et al.*[3]

Lifetimes due to valence electrons can be calculated according to $\lambda_{val}\equiv1/\tau_{val}=1/\tau_B-\lambda_c$, when using λ_c from the work of Puska *et al.*[3] The free-electron model predicts a near-proportional increase of lifetime with r_s^3, i.e., with the inverse of the valence-electron density. In Fig. 2 we find this also to be the case for semiconductors. Thus, as far as positrons are concerned, the free-electron model for the valence electrons explains well general trends of S_{val} and τ_{val}. From the above it follows that τ_{val} is proportional to the third power of S_{val}.

The fact that valence electrons are bonded shows up in directional anisotropies which are clearly observable from the more discriminating angular correlation experiments,[8] and which are predicted from theoretical calculations.[9] Anisotropies are barely observable by Doppler broadening, as shown in Table III in the case of silicon (the only material investigated for this purpose).

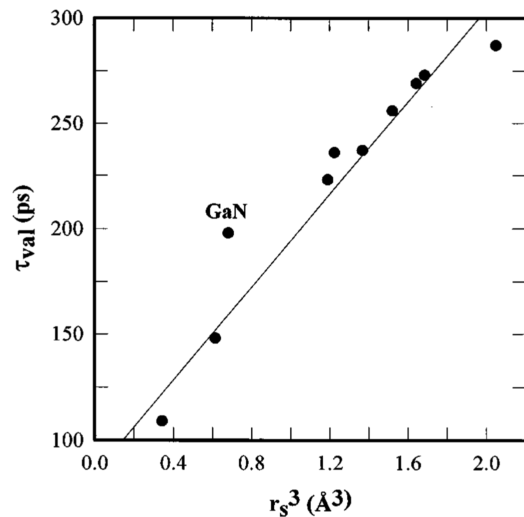

FIG. 2. Positron lifetimes (at room temperature) due to valence electrons as a function of r_s^3. The large value for GaN arises because of an uncharacteristically large contribution from the core contribution.

TABLE III. Anisotropy of S_{expt} values for Fz-Si for three crystallographic directions.

hkl	[100]	[110]	[111]
$S_{hkl}/S_{[100]}$ (± 0.001)	1	1.007	1.005

So far we have not considered the W_{expt} parameter. This parameter cannot reasonably be correlated with r_s, because W_{expt} depends heavily on core annihilations to which r_s is not related. We would, though, caution against the view that W_{expt} and S_{expt} are complementary, i.e., that an increase in W_{expt} is reflected in a proportional decrease in S_{expt}. We demonstrate the reason for this caution in Fig. 3 by plotting S_{expt} versus W_{expt}. Although most of the data points can be seen to correlate, albeit not linearly, the data for Si and SiC clearly deviate from the ''main'' trend.

We now turn to the temperature dependencies of S_{expt}. In order to facilitate comparisons between the various samples, the parameter $\Delta S = S_{expt}(T) - S_{expt}$ (100 K) is plotted in Figs. 4–7. The changes in ΔS with temperature are reversible, but are on a much smaller scale than those dealt with so far; for such small changes it is doubtful that the crude r_s-based model would be applicable when dealing with thermal-expansion effects.

Although ΔS increases monotonically with temperature [except for the case of GaP, Fig. 7(b)], it is clear that in the 100–300-K range the behavior of ΔS is sample dependent, while between 300 and 600 K linear increases are observed for all samples. In the latter temperature range the thermal-expansion coefficient is essentially temperature independent,[10] suggesting the increase in ΔS to be caused by thermal expansion. To see if there exists a simple relation between ΔS and the thermal-expansion coefficient α, the ratio $\beta = \gamma/\alpha$ is a relevant parameter, where γ is the slope of ΔS versus temperature. Using data for α from Refs. 11 and 12, values of β are shown for each straight-line segment in Figs. 4–7. The scatter in the values of β between the different materials (for example, β_{Si} equals 0.6, and β_{InSb} equals 1.4) demonstrates a complex temperature dependence, one source of which may be core contributions which differ from sample to sample. In the cases of GaAs (Fig. 5) and InP (Fig. 6) doping has some influence on the values for β.

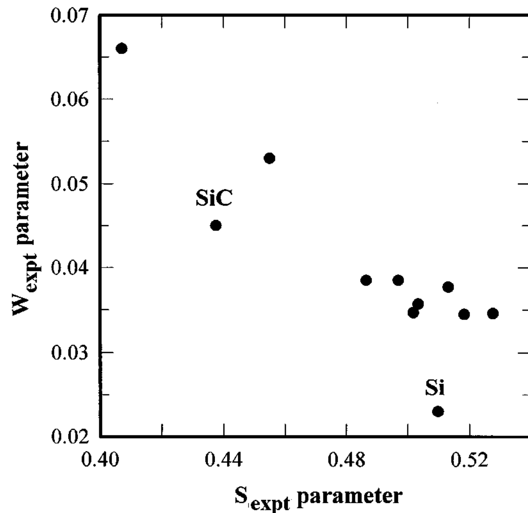

FIG. 3. Experimentally determined W_{expt} values plotted vs the S_{expt} parameter.

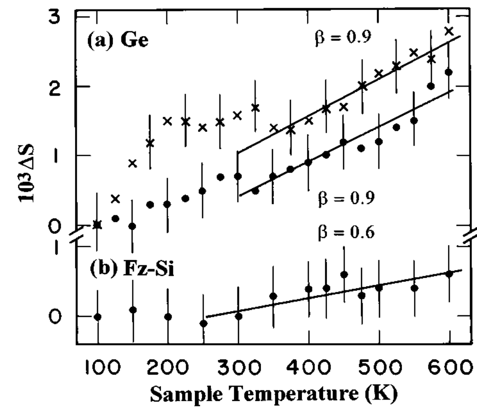

FIG. 4. Temperature dependence of $\Delta S = S_{expt}(T) - S_{expt}$ (100 K). (a) 1-Ω cm Ge (×) and 50 Ω cm (●). (b) Undoped Fz-Si. The straight-line segments in (a) and (b) indicate the basis on which the temperature dependence of ΔS is evaluated in the 300–600-K temperature range. β equals the ratio between the slope of ΔS and the thermal-expansion coefficient.

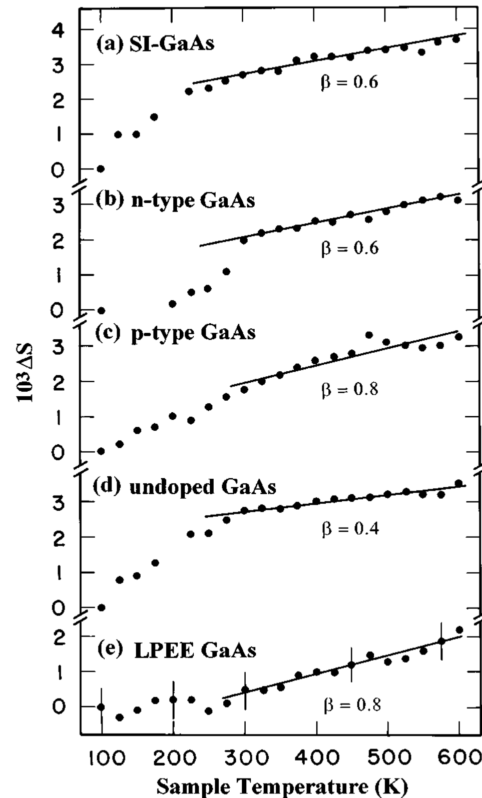

FIG. 5. Temperature dependence of ΔS for various GaAs samples. Straight-line segments approximate ΔS above 300 K. In (e), LPEE GaAs is a liquid-phase electroepitaxially grown GaAs with an exceptionally low vacancy concentration (see Ref. 16). β equals the ratio between the slope of ΔS and the thermal expansion coefficient.

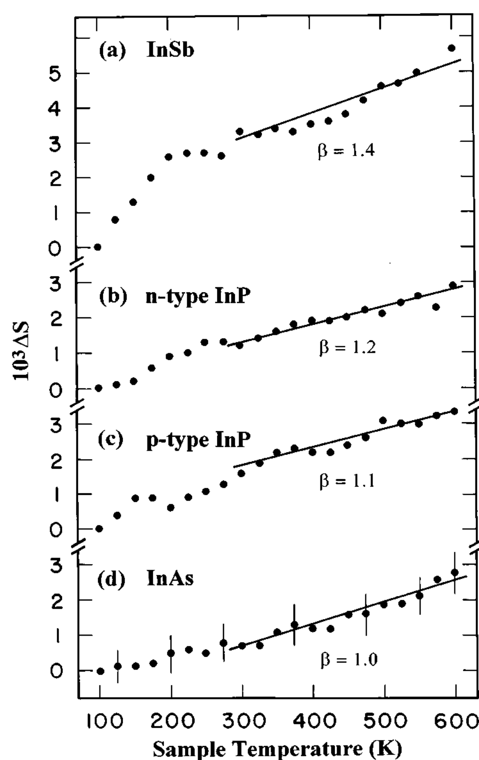

FIG. 6. Temperature dependence of ΔS for (a) InSb (n type, undoped), (b) and (c) two types of InP, and (d) InAs (n type, undoped). β equals the ratio between the slope of ΔS and the thermal-expansion coefficient.

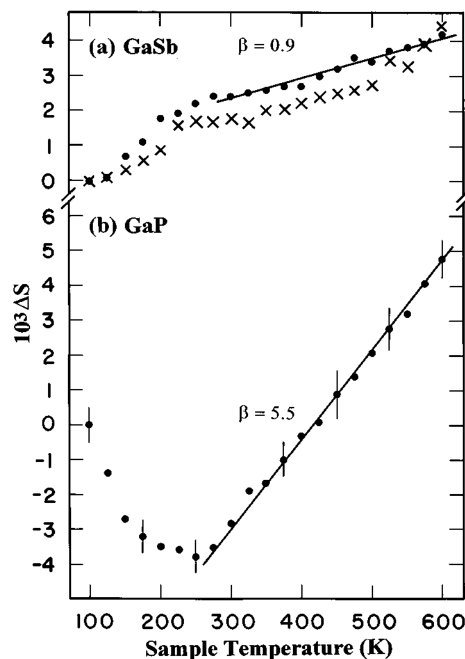

FIG. 7. Temperature dependence of ΔS for (a) GaSb (n type: two samples from different wafers from the same ingot), and (b) GaP (n type, S doped). β equals the ratio between the slope of ΔS and the thermal-expansion coefficient.

The exceptionally large value of β for GaP is most likely due to extrinsic effects, a possibility which is qualitatively supported by the observed large differences in S_{expt} for S- and Zn-doped GaP (see the caption to Table I).

Between 100 and 300 K the sample dependency of the changes in ΔS (most clearly shown in the case of GaAs) suggests contributions which might be of extrinsic nature. These could conceivably arise from defects whose presence is indicated by the lifetime data in Table II. In the case of GaAs, Kerr, Kupca, and Hogg[13] and Saarinen *et al.*[14] found that the amount of positrons trapped by vacancies increased with temperature, which would increase ΔS and so add to whatever the intrinsic thermal effects might be.

IV. CONCLUSIONS

A survey of 11 semiconducting materials, spanning a large range of electron densities, has confirmed the theoretical model of Brandt and Reinheimer[1] that positrons probe valence electrons as if these electrons were free. Only slight anisotropies in the Doppler S_{expt} parameter reflect the actual bonded nature of the valence electrons.

Temperature effects were investigated by means of Doppler broadening. Changes in S_{expt} above 300 K were linear, suggestive of lattice-expansion effects. At temperatures below 300 K, changes in S_{expt} are sample dependent, which is suggestive of the presence of grown-in defects.

ACKNOWLEDGMENTS

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