It is convenient to express the coefficient  $A_{rl}$  in the Substituting Eq. (A8) into Eq. (A1), using the fact that form

$$
A_{rl} = [l+r]^2 [(l+r)^2 - 1] [(l+r)^2 - 4] \cdots
$$
  
 
$$
\times [(l+r)^2 - (r-1)^2].
$$
 (A6)

Then, setting  $(l+r)=n$  in the right side of Eq. (A4) we have

$$
\frac{(2r)!}{(r!)^2 2^{2r+1}} \alpha_s^{2r} = \sum_{n=r}^{\infty} n^2 (n^2 - 1) (n^2 - 4) \cdots
$$
\n
$$
\times (n^2 - (r-1)^2) J_n^2(\alpha_s). \quad (A7)
$$
\n
$$
I_s(V) = \sum_{r=0}^{\infty} \frac{(-1)^2}{(r!)^2} \frac{1}{2} \cdots \frac{1}{dV^{2r}}
$$
\n
$$
(A9)
$$
\nor\n
$$
I_s(V) = I_0(\delta[cs] d/dV) I(V), \quad (A10)
$$

The lower limit on the summation in Eq. (A7) can be replaced by  $n=0$ . We then have (for  $r>0$ )

$$
\sum_{n=0}^{\infty} X_n n^{2r} J_n^{2}(\alpha_s) = \frac{(2r)!}{(r!)^2 2^{2r}} \alpha_s^{2r} + \text{terms proportional}
$$
  
to  $\alpha_s^{2r-2}$ ,  $\alpha_s^{2r-4}$ , etc. (A8)

$$
\sum_{n=0}^{\infty} X_n J_n^2(\alpha_s) = 1
$$

and taking the limit  $\alpha_s = (\delta(\cos)/\hbar\omega) \rightarrow \infty$ , one easily obtains the following result for  $I_s(V)$ :

$$
I_s(V) = \sum_{r=0}^{\infty} \frac{1}{(r!)^2} \left(\frac{\left[\delta(c_s)\right]}{2}\right)^{2r} \frac{d^{2r}I(V)}{dV^{2r}} \tag{A9}
$$

$$
I_{s}(V) = I_{0}(\delta \big[ cs \big] d/dV) I(V), \qquad (A10)
$$

where  $I_0$  is the modified Bessel function of order zero.

Note added in proof. It has now been established that the high  $T_c$  of the aluminum films used in the present work results from contamination by oxygen. The effect of oxygen on the  $T_c$  of metal films is described by B. Abeles, R. W. Cohen, and G. W. Cullen in Phys. Rev. Letters 17, 632 (1966).

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# Decay Features of Positrons in Semiconductors\*

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Positron lifetime measurements in some typical semiconductors are reported. In every case the decay displays two components, the longer one being of the order of  $\tau_2=10^{-9}$  sec and having an intensity of a few percent. Measurements on neutron-damaged samples show that both components are sensitive to the presence of lattice defects. Moreover, at least in the case of silicon, the long-lifetime component is lacking when a high electric field is applied to the sample. Also, the presence of a high oxygen concentration in gallium arsenide and in silicon is effective in preventing annihilations through the  $\tau_2$  lifetime.

## INTRODUCTION

POSITRON lifetime measurements in germanium<sup>1</sup> established that the decay is simple, displaying only one lifetime; moreover, the shape of angular correlation spectra in germanium and silicon, $2^{-4}$  substant ally an inverted parabola, led to the conclusion that positrons annihilate with nearly free electrons, without formation of positronium-like bound states. On the basis of these results, one could suppose that positron annihilation in semiconductors is likely to display features similar to those in metals. However, in semiconductors it is possible to make the conduction-electron concentration vary over a wide range, both by doping the samples

and, in nonequilibrium conditions, by applying an electric field to them.

It seems therefore worthwhile to examine positron decay features in a few typical semiconductors; silicon, germanium, boron, gallium arsenide, and silicon carbide have been tested.

### EXPERIMENT AND RESULTS

The Vernier time sorter has already been described in previous work.<sup>5</sup> The over-all resolution defined by the full width at half-maximum of a prompt-coinciden<br>curve was  $8.5 \times 10^{-10}$  sec. curve was  $8.5 \times 10^{-10}$  sec.

The source, about 20  $\mu$ Ci of carrier-free Na<sup>22</sup>, was deposited directly onto the samples, which were in the shape of disks cut from single crystals, except for boron and silicon carbide, which were polycrystalline.

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<sup>\*</sup><sup>A</sup> few preliminary results from this study have been presented at the Positron Annihilation Conference, Detroit, 1965.<br>
<sup>1</sup>G. Jones and B. Warren, Can. J. Phys. 39, 1520 (1961).<br>
<sup>2</sup>G. Lang and S. De Benedetti, Phys. Rev. 108, 914 (1957).<br>
<sup>3</sup>A. T. Stewart, Can. J. Phys. 35, 168 (1957

<sup>950</sup> (1964).

<sup>&</sup>lt;sup>5</sup> E. Germagnoli, G. Poletti, and G. Randone, Phys. Rev. 141, 419 (1965).

 $10<sup>1</sup>$ 

 $10<sup>10</sup>$ 

Counting rate

	$\tau_1$ (10 <sup>-10</sup> sec) $\tau_2$ (10 <sup>-9</sup> sec)		$I_2(\%)$
Silicon	$2.6 + 0.3$	$1.2 + 0.05$	$2.6 + 0.5$
Germanium	$2.4 + 0.5$	$1.9 + 0.05$	$1.6 + 0.5$
<b>Boron</b>	$3.5 + 0.5$	$1.9 + 0.05$	$2.8 + 0.5$
Gallium arsenide	$2.8 + 0.5$	$2.1 + 0.05$	$2.3 + 0.5$
Silicon carbide	$2.2 + 0.5$	$1.8 + 0.05$	$1.3 + 0.5$

TABLE I. Experimental results.

The silicon, germanium, and gallium arsenide samples were differently doped. Silicon and germanium were doped  $\nu$ -type with boron and *n*-type with phosphorus in such concentrations that the resistivity ranged from 1  $\Omega$ cm to  $2\times10^4$  Ω-cm in the case of silicon, and from 0.3  $\Omega$ -cm to 50  $\Omega$ -cm in the case of germanium. Gallium arsenide was doped *n*-type with tellurium and  $p$ -type with zinc; in both cases the resistivity was about  $0.1 \Omega$ cm.

Figure 1 shows four typical delay spectra and Table I collects the experimental results.

A general feature of the delay spectra is that the shape of the curves depends only on the material, not on the doping; and in every case the decay displays two components, the longer one, of the order of  $10^{-9}$  sec, having an intensity of a few percent.

With the aim of checking a possible correlation between positron-annihilation features and lattice defects, samples of silicon, germanium, and gallium arsenide have been heavily damaged with an integrated neutron flux of about  $2 \times 10^{18}$  n/cm<sup>2</sup>. Of course the measurements were performed after the induced radioactivity decreased to such low intensities as to prevent spurious pulses from being recorded in the analyzer. Table II collects the results concerning irradiated samples.

Owing to the low intensity of the  $I_2$  component it is difficult to draw any definite conclusion about correlations between lattice defects and the long-lifetime component; only a systematic increase in the short lifetime can be pointed out. On the other hand, as mentioned above, doping does not affect the annihilation features; that is, positrons are insensitive to the equilibrium concentration of the conduction electrons. Therefore it looks reasonable to conclude that the electron density that the positron experiences is substantially due to valence electrons and to the electrons raised in the conduction band by the positron itself. Nevertheless, it is possible to reduce the latter contribution to a negligible level by applying to the sample a high enough electric field to sweep the excited electrons away from the positron in a time which is short in comparison

TABLE II. Results for irradiated samples.

	$\tau_1$ (10 <sup>-10</sup> sec) $\tau_2$ (10 <sup>-9</sup> sec)		$I_2(%)$
Silicon	$3.6 + 0.5$	$1.3 + 0.1$	$1.5 + 0.5$
Germanium	$3.8 + 0.5$	$1.9 + 0.05$	$1.5 + 0.5$
Gallium arsenide	$3.5 + 0.5$	$1.8 + 0.5$	$0.5 + 0.5$

10  $10$ Boron Silicon Carbide

'n

.<br>Permanium

 $(x 10)$ 

.<br>Sallium Arsenide

 $(x10)$ 

FIG. 1. Typical delay spectra (1 channel =  $1.5 \times 10^{-10}$  sec).

with the annihilation lifetime. The case of silicon is the most favorable because it is possible to record the delay spectrum of positrons annihilating in the space-charge region of silicon detectors. For the measurements, surface-barrier silicon detectors were used because in the preparation of such a device there are no operations that can modify the bulk properties of the single crystal with which one starts; furthermore, in these semiconductor detectors, the dead layer does not exceed thicknesses equivalent to 40–50  $\mu$ g/cm<sup>2</sup>, corresponding to a negligible energy lost by the positron.

The measurements were performed with semiconductor detectors prepared starting with  $n$ -type silicon, the resistivity of which was 1800  $\Omega$ -cm; with a reverse bias of 400 V, the thickness of the depletion layer is about  $430 \mu$ . Taking into account the mean electric field strength ( $\sim$ 10<sup>4</sup> V/cm) and electron mobility in silicon, it is possible to conclude that an electron, excited to the conduction band by a positron, gets a few microns away from the positron itself in a time which is very short in comparison with the annihilation lifetime.

The positron source was deposited in a small cavity carved in an  $n$ -type silicon single crystal which was placed in front of the sensitive area of the surfacebarrier silicon detector.

A block diagram of the experimental arrangement is shown in Fig. 2. Detectors  $A$  and  $B$  were NE 102 plastic



FIG. 2. Block diagram of the experimental arrangement. P.A.=pulseheight analyzer.

scintillators; detector  $C$ , the surface-barrier silicon junction connected to a fast amplifier and detecting the positrons.

Pulses from detectors  $A$  and  $B$ , with suitable amplitude requirements, were fed into the vernier time sorter for delay measurements, the delay spectrum being stored within the first 100 channels of a 200-channel pulse-height analyzer.



FIG. 3. Delay spectra of positrons annihilating in  $n$ -type silicon single crystal and in the space-charge region of a silicon surfacebarrier detector.

Channels  $A$ ,  $B$ , and  $C$  are connected to a threefold fast coincidence circuit, the output of which allows pulses from the time-sorter to be stored in the second 100 channels of the analyzer.

Figure 3 shows the delay curves measured by the experimental apparatus described. The lack of a tail with the long lifetime  $(\tau_2)$  is evident in the curve describing the annihilation in the space-charge region of the detector. No influence of the electric field on the short lifetime is evident.

In the case of a 1800- $\Omega$ -cm detector, the applied voltage was limited on the low side by the requirement that the space-charge region should be thick enough to stop all the incoming positrons. To evaluate the lowest electric field necessary to display the above-mentioned effect, experiments have been done with silicon detectors of the highest resistivity at our disposal, namely  $2.1 \times 10^4$  $\Omega$ -cm; here the mean applied field was about 10<sup>3</sup> V/cm; but again the delay spectrum was indistinguishable from the one previously recorded with the  $1800 - \Omega$ -cm detector.

Unfortunately the other semiconductors considered in the present work do not allow one to repeat the same experiment, because for some of them no technique to obtain a  $p$ -*n* junction is available; for others it is impossible to make junctions which, with reverse bias, give a depletion layer thick enough to stop positrons from Na<sup>22</sup>. Therefore the only possibility was to investigate the effect of the electric field on those semiconductors the resistivity of which could be raised to such high values as to allow the direct application of a static electric field. Among the tested materials this possibility was confined to gallium arsenide, which, by oxygen compensation, may be obtained with a resistivity of the

order of  $10^6$   $\Omega$ -cm. The delay spectrum of oxygencompensated gallium arsenide surprisingly does not display any long-lifetime tail. Anyway, the measurement has been performed. The presence of an electric field of about  $10^4$  V/cm had no evident influence on the delay spectrum of high-resistivity gallium arsenide. The lack of a long-lifetime tail in the curve describing compensated gallium arsenide can be qualitatively related to the presence of oxygen. It seemed therefore worth while to make a measurement in a silicon single-crystal sample into which a high oxygen concentration had been dissolved during the growth. The experimental result of a measurement in a silicon sample in which the oxygen concentration (measured by infrared absorption technique) was about  $10^{18}$  atoms/cm<sup>3</sup>, displayed the same surprising lack of any appreciable long-lifetime component, as shown in Fig. 4.

#### **DISCUSSION**

A general conclusion which can be drawn from the experimental results concerning samples of the same material differently doped is that positron-decay features are not affected by the equilibrium concentration of conduction electrons. Therefore it is conceivable that the conduction-electron density at the positron is substantially yielded by electrons raised to the conduction band by the positron itself. In particular, the bound state associated with the  $\tau_2$  component can be formed only with conduction electrons, because the  $\tau_2$  tail is lacking when annihilations happen in silicon junctions, where the electric field sweeps away the excess electrons.

On the other hand, an electric field has no appreciable influence on the short-lifetime component.

Nevertheless, it seems reasonable to suppose also that the short-lifetime component does not come only from free annihilations, since the measurements on neutrondamaged samples systematically show an increase in the  $\tau_1$  lifetime. As far as the radiation effect on the  $\tau_2$ component is concerned, it can be noted that the  $\tau_2$ tail becomes negligible in gallium arsenide, while in silicon it decreases and in germanium it does not change significantly; but, because of the disorder from substitutions, radiation damage is more effective in binary than in elementary compounds and the correlation with the  $\tau_2$  tail does not seem fortuitous.



FIG. 4. Delay spectra in oxygen-doped silicon and gallium arsenide.

Moreover, a high oxygen concentration in gallium arsenide and silicon is effective in preventing annihilations through the  $\tau_2$  lifetime. Although the mechanism by which oxygen raises the gallium arsenide resistivity to such high values is not well known, it seems unlikely that the oxygen electron configuration is the same in the silicon and in the gallium-arsenide lattice. Nevertheless, oxygen affects the  $\tau_2$  component in the same way in both cases. Therefore one is led to suppose that both in the silicon sample and in the gallium arsenide sample, oxygen clusters are present in addition to substitutional oxygen atoms, and the clusters may be responsible for the lack of a  $\tau_2$  component.

In principle it would be interesting to study the behavior of the  $I_2$  tail intensity as a function of oxygen concentration, but such measurements would be unreliable from an experimental point of view, owing to the low intensity of the  $I_2$  component even in very pure samples.

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