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SURFACE EFFECTS ON POSITRON ANNIHILATION IN SILICON POWDERS*

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Positron lifetime measurements were made in silicon powder samples with different grain size and doping. Two lifetime components were detected in low-resistivity *n* samples and in high-resistivity *p* samples having grain sizes smaller than about 50 μ. The faster component [$\tau_1 = (2.59 \pm 0.10) \times 10^{-10}$ sec] was easily ascribed to annihilations in the bulk; the slower one [$\tau_2 = (5.20 \pm 0.20) \times 10^{-10}$ sec] was ascribed to annihilation processes taking place in the oxide surface layer.

Positron-lifetime spectra in silicon single crystals have been extensively studied by several workers[1-4] and are commonly interpreted in terms of a single significant decay component τ_1 which appears to be independent of the type and the amount of doping. The lifetime τ_1 was found to depend strongly on the mean valence-electron density and the polarizability of the valence band, and was then ascribed to annihilations with the electrons of the valence band.[4] In this paper we report positron-lifetime measurements in silicon powder samples where a slower decay component τ_2 is also observed. The experimental data suggest that this new component τ_2 is due to annihilation processes which take place near the surfaces of the grains.

The experimental technique for the recording and analysis of the lifetime spectra has been described previously.[4] With narrow energy-selection windows set near the Compton edges of the Na^{22} spectrum, the full width at half-maximum (FWHM) of the prompt time-resolution curve taken with the γ rays emitted by Co^{60} was 3.5×10^{-10} sec. The peak-to-background ratio was 10^4:1.

First we measured the positron lifetime in a single-crystal sample. The same single crystal was then powdered in atmospheric air in order to obtain several powder samples of different grain sizes. The mean diameter of the powder grains was measured by means of an optical microscope, and finally positron-lifetime spectra of each sample were taken. In order to avoid the presence of dust and humidity, all lifetime measurements were taken in a vacuum (10^{-4} Torr). The whole process was carried out for (a) *n*-type samples with 2×10^{18} Sb atoms/cm^3, (b) *p*-type samples with 3×10^{18} B atoms/cm^3, and (c) *p*-type samples with 8×10^{14} B atoms/cm^3. In all three cases we started with single-crystal samples where only one significant lifetime $\tau_1 = (2.62 \pm 0.015) \times 10^{-10}$ sec was detected; a second tail component was also present with a maximum intensity of 2.7% and a lifetime ranging from 5.3×10^{-10} to 14.8×10^{-10} sec. This latter component may be ascribed to spurious effects as was explained in previous works.[3,4]

In powder samples we found identical results as for single crystals when we examined samples having grain size greater than about 50 μ. Then, in case (a) the abrupt appearance of a slower decay component τ_2 [with lifetime $\tau_2 = (5.20 \pm 0.20) \times 10^{-10}$ sec] was observed. Subsequently the intensity I_2 of the new component showed a slow increase with decreasing grain size up to 25% for grain sizes of about 2-3 μ.

In Fig. 1 a typical decay spectrum is reported where the slower component is clearly evidenced. The effect is considerably less marked in case (b), and no one significant τ_2 component was observed in low-resistivity *p*-type samples [case (c)]. Finally, it must be pointed out that the τ_1 fast component was always detected in all powder samples with an averaged lifetime [$\tau_1 = (2.59 \pm 0.10) \times 10^{-10}$ sec] which is, significantly, equal to the single-crystal lifetime and can therefore be ascribed to the same annihilation process which was assumed for single crystals.

The first suggestion is that the slow component is due to positrons which annihilate near the grain surfaces, being captured by a surface potential well. Then, following Brandt and Paulin,[5]

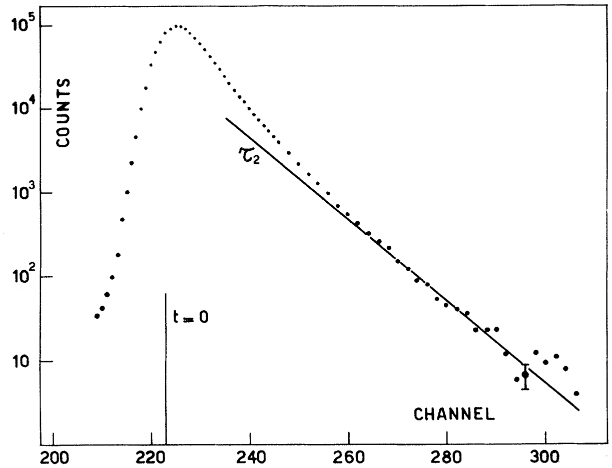

FIG. 1. Positron-decay spectrum in n-type silicon powder sample (2×10^{18} Sb atoms/cm^3; grain size 2.5 μ). $\tau_2=(5.16\pm0.12)\times10^{-10}$ sec; $I_2=(24.4\pm1.5)\%$. One channel $=0.61\times10^{-10}$ sec.

if one assumes that positrons can become thermalized with an equal probability at every point inside a grain, the probability of a positron to reach the surface by a random-walk path is given by

$$\Phi=\tfrac{3}{2}\beta\left[1-\beta^2+(1+\beta)^2e^{-2/\beta}\right], \tag{1}$$

with $\beta=(D\tau_1)^{1/2}/R$, where R is the grain radius and D is the diffusion constant. D and τ_1 are related to the mean path Λ in the grain before annihilation by

$$\Lambda/\sqrt{2}=(D\tau_1)^{1/2}. \tag{2}$$

Φ is a continuously increasing function with decreasing grain radius and starts in a nearly linear way, with derivative $\frac{3}{2}$, for small values of β. This behavior is somewhat in contrast to the experimental data which are summarized in Fig. 2, where the intensity I_2 is plotted against the logarithm of $1/R$. The fact that I_2 is undetectable for values of R greater than about 25 μ is not explained by relation (1) and seems to require the phenomenological hypothesis that positrons thermalize mainly near the centers of the grains. If so, a positron would require a long time about R^2/D in order to reach the surface; then if $R^2/D \gg\tau_1$, the positron has a high probability of annihilation before reaching the surface. However this hypothesis seems hardly justifiable, and in any case the mechanism for a positron to reach the surface must be better clarified with theory and experiments.

We may assume that the surface potential well's capture of positrons is due to the presence of the oxide layer. This is supported by the fact that the lifetime τ_2 of the slower component is nearly the same as the most intense decay component τ_1 in SiO$_2$. Results on positron lifetime in SiO$_2$ powders (99.9999 %) are as follows: $\tau_1=(5.7\pm0.2)\times10^{-10}$, $\tau_2=(24\pm3)\times10^{-10}$ sec; $I_2=11\pm2\,\%$; $\tau_3=(150\pm20)\times10^{-10}$ sec; and $I_3=10\pm1\,\%$. Small differences between τ_2 (silicon powders) and τ_1 (SiO$_2$) may be due to the fact that we measured positron lifetimes in crystalline samples of SiO$_2$ rather than in amorphous ones. If this hypothesis is correct, we may expect that positrons experience a potential $V(r)$ like that in Fig. 3. The potential is that which would be experienced by a free electron, with the only modification being that the sign of grad $V(\vec{r})$ is now reversed in order to take account of the positive sign of the positron charge. So, in intrinsic samples, V_0 is the semidifference of the widths of the forbidden energy gaps of SiO$_2$ and of silicon; that is, V_0 is of the order of an electron volt.

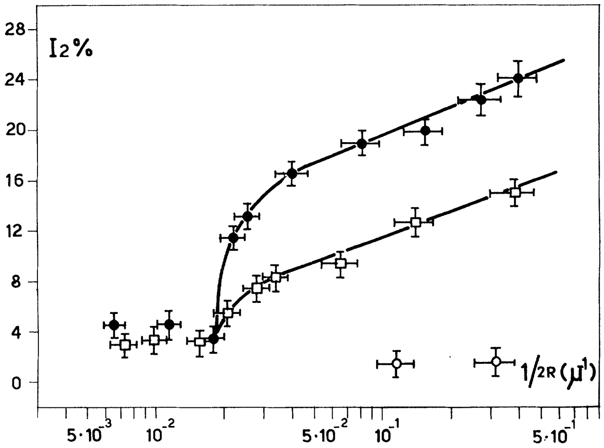

FIG. 2. I_2 versus $\ln(1/2R)$: Solid circles, low-resistivity n samples [case (a)]; open squares, high-resistivity p samples [case (b)]; open circles, low-resistivity p samples [case (c)]. I_2 values corresponding to values of $1/2R$ lower than about $2\times10^{-2}\ \mu^{-1}$ are consistent with lifetime values which may differ considerably from the value 5.20×10^{-10} sec. No one physical significance may be assigned in this case to the τ_2 component (as for single-crystal samples). The same argument holds for low-resistivity p samples where the I_2 values reported above are consistent with lifetime values of 8.4×10^{-10} sec ($1/2R=0.113\ \mu^{-1}$) and 7.3×10^{-10} sec ($1/2R=0.312\ \mu^{-1}$).

The energy of the positron in the vacuum is taken to be greater than inside the grain, so that a thermalized positron is supposed to be unable to escape out of the grain. However the height of this potential barrier is sketched in Fig. 3 in an

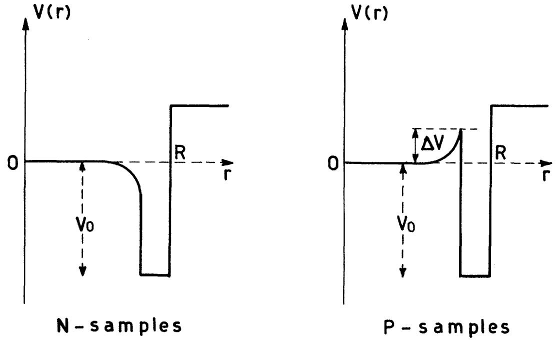

FIG. 3. Qualitative sketch of the potential $V(r)$ experienced by a positron inside a grain. The grain is supposed to have a spherical shape with diameter $2R$; r is the distance from the center of the grain.

arbitrary way because of the lack of computations and of conclusive experiments about the positron affinity in solids. The periodic lattice potential is neglected both in the bulk and in the oxide layer: This is justified for Si where positron annihilation data are commonly interpreted in terms of free annihilations, but not in SiO_2 where one may expect positrons to annihilate mainly in bound states with one or more O^{--} ions. The amount and sign of the bending of $V(r)$ near the oxide-semiconductor interface are controlled by the distribution of fast surface states and by the position of the Fermi level.

A fully satisfactory explanation of the experimental results can be given only if the distribution and the nature of fast states may be detected by some other independent technique. Unfortunately this is quite a difficult task, as we know, to perform in powder samples. However, if both donor and acceptor fast states have a constant distribution over the entire energy gap, the situation is qualitatively similar to that sketched in Fig. 3. The same situation is also highly probable in low-resistivity samples, whatever the distribution of fast states, because the position of the Fermi level practically excludes the possibility for either donor or acceptor states being occupied. In p samples the positive sign of the surface charge clearly prevents a thermal positron from being captured by the oxide potential well. In fact the surface bending ΔV of $V(\vec{r})$ is of the order of $(eN_s^2/2\epsilon N_a)$, where ϵ is the dielectric constant, N_s the number of available donor surface states per unit area over the Fermi level, and N_a the acceptor concentration. For high-resistivity samples, N_s may be assumed to be of the same order of surface-state concentration; that is, for real surfaces N_s may be of the order of 3×10^{12} cm^{-2}.[6] Then, with $\epsilon \sim 16\epsilon_0$ and with $N_a = 3\times10^{18}$ atoms/cm^3, we have $\Delta V \simeq 0.17$ V which corresponds to an energy much greater than KT. The contrary happens in n samples, so the fact that in low-resistivity p samples [case (c)] no one significant slow component was observed is well explained. The I_2 intensity detected in high-resistivity p samples, though smaller than in n-type powders, suggests a nonuniform distribution of fast states through the forbidden-energy gap: In this case the sign of the surface-charge layer becomes very sensitive to the fast-state distribution because the Fermi level is placed not very distant from the intrinsic position.

As a final remark it must be pointed out that the slow component lifetime τ_2 practically coincides with the lifetime of the 1s positronium atom averaged over random spin orientations (4.98×10^{-10} sec).[7] One might thus suppose that positronium is formed in the interstitial regions between the grains; if so, the whole matter would be doubtful. However this last hypothesis may be discarded for two reasons: first, because it would require a complete rapid triplet-singlet conversion, and second, because a negative positron affinity for the oxide layer would be required for a thermal positron to excape out of a grain.

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