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Diffusion of Positrons to Surfaces

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Abstract. Low-energy positrons implanted into a crystal can diffuse to the surface where they may be detected, for instance, by observing the formation of positronium. We describe the positron motion by a one-dimensional diffusion equation, and discuss the measurement of vacancy activation energies, positron diffusion constants, and positron stopping profiles.

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There is considerable interest in the study of low-energy positrons interacting with solid targets in vacuum [1]. In recent experiments a beam of positrons with well defined energy strikes a clean single crystal surface. The energy spectrum of the resulting annihilation photons yields information about positronium formation [2, 3], slow positron emission [4] and positron surface states [5–7]. In particular, if these surface effects are studied as a function of the positron incident energy, one can learn about the diffusion process by which the positrons reach the surface of the sample after being implanted into the bulk. The motion of the positrons in the bulk appears to be fairly well described by a one-dimensional diffusion equation

$$\dot{\varphi}=D\partial^2\varphi/\partial x^2-\gamma\varphi, \tag{1}$$

where φ is the density of positrons in the material, D is the positron diffusion constant and γ is the rate of decay due to annihilation and trapping. The experiments yielded values of D in metals and have shown a high sensitivity to the presence of defects close (~ 1000 Å) to a surface. It is the possibility of measuring vacancy activation energies in thin samples [8] and of quantitatively detecting other crystalline imperfections in surface layers that makes it desirable to discuss the use of (1) in more detail.

For completeness we first present the derivation of an expression giving the fraction of positrons reaching a surface after being implanted. The derivation of this formula was also given by Lynn and Welch [9], and may be found in the monograph by Bell [10]. We then discuss the application of the formalism to the measurement of positron diffusion constants and trapping rates.

Model and its Application

In experiments on semiconductors there may be internal electric fields $\mathbf{E}$ near the surface which can influence the positron diffusion. These electric fields can be produced either by doping the crystal or by applying a voltage across electrodes plated on the surface. In either case it is interesting to see how the positron diffusion will be modified. The equation we must solve is [10]

$$\dot{\varphi}=D\nabla^2\varphi-\mu\mathbf{E}\cdot\nabla\varphi-\gamma\varphi, \tag{2}$$

where μ is the positron mobility in the crystal.

Given that positrons have been implanted into a solid surface with some distribution $P(x)$ vs depth x at the initial time $t=0$, our problem is to calculate how many of the positrons diffuse to the surface at $x=0$ before annihilating or being trapped in the bulk. At the surface we suppose that there is a perfectly absorbing boundary such that $\varphi=0$ for $x<0$; more general boundary conditions were discussed by Lynn and Welch [9], by Bell [10], and by Oliva [11]. Solutions satisfying the boundary condition are

$$\varphi_k(x,t)=\theta(x)\sin(kx)\,e^{\lambda x}\,e^{-\alpha t}, \tag{3}$$

where $\lambda=\mu E/2D$, $\alpha=D(k^2+\lambda^2)+\gamma$, $\mathbf{E}$ is a constant electric field pointing in the $\hat{x}$ direction, $\theta(x)$ is the unit

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step function and $k>0$. The general solution is a linear combination of φ_k's

$$\psi(x,t)=\int B(k)\,\varphi_k\,dk\,, \tag{4}$$

where the amplitudes $B(k)$ for a δ-function initial distribution at $x=a$, $\psi(x,0)=\delta(x-a)$, are

$$B(k)=\frac{2}{\pi}\sin ka\,e^{-\lambda a}\,. \tag{5}$$

The quantity which may be determined experimentally is the total fraction of particles lost through the boundary. This is given by

$$L(a)=\int_0^\infty D\frac{\partial}{\partial x}\psi(x,t)\Big|_{x=0+}dt=e^{-\xi a}\,, \tag{6}$$

where $\xi\equiv\sqrt{\gamma/D_{\rm eff}}=\sqrt{\lambda^2+\gamma/D}+\lambda$. We see that an internal electric field results in an $L(a)$ which appears to be associated with an effective diffusion constant $D_{\rm eff}$. Internal fields can therefore only be calculated from $L(a)$ if we know the actual diffusion constant D from independent measurements.

Since the incident positrons are not all deposited at the same depth we average $L(a)$ over the stopping profile $P(a)$ to obtain an expression which can be compared with experiment: $\bar{L}=\int_0^\infty P(a)L(a)da$. For electrons, Makhov [12] has parameterized the stopping profile by

$$P(a)\propto a^{\alpha_1}\exp(-\alpha_3 a^{\alpha_2}) \tag{7}$$

and found $\alpha_1=1, \alpha_2=2$ fits most of his data while $\alpha_1=0$, $\alpha_2=1$ fits one set of data. Oliva [11] has calculated $P(a)$ for positrons in jellium. We are presently not certain of the correct form of $P(a)$. However, an exponential stopping profile $P(a)=\bar{a}^{-1}\exp(-a/\bar{a})$ is a convenient first approximation which leads to a simple expression for the fraction of the incident positrons which reach the surface before annihilating or trapping in the bulk:

$$\bar{L}(\bar{a})=(\xi\bar{a}+1)^{-1}\,. \tag{8}$$

For $E\gg 0$, $\xi\to\infty$ and $\bar{L}(\bar{a})=0$ while for $E\ll 0$, $\xi\to 0$ and $\bar{L}(\bar{a})=1$ corresponding to the escape from the surface of all the incident particles. If we assume that the mean stopping length $\bar{a}$ is proportional to the incident positron energy W, $\bar{a}=AW$, (8) provides a reasonably good representation of the experimental results [2, 3].

Making use of the Nernst-Einstein relation $D=\mu kT/e$, λ can be expressed as $eE/2kT$, and the inverse effective diffusion length ξ becomes

$$\xi=\left(\frac{\gamma}{D_{\rm eff}}\right)^{1/2}=\frac{eE}{2kt}+\left[\left(\frac{eE}{2kT}\right)^2+\frac{\gamma}{D}\right]^{1/2}. \tag{9}$$

Typical electric fields at doped semiconductor surfaces due to band bending caused by electronic surface states are on the order of 10^3–10^5 V/cm, making λ comparable in magnitude to $(\gamma/D)^{1/2}$ at room temperature, $\sim 10^5\,{\rm cm}^{-1}$ for Ge [13]. Thus surface accumulation or depletion layers can cause a large effect in the measured $D_{\rm eff}$. As the band bending is a function of temperature, $D_{\rm eff}$ may also have a complicated temperature dependence in doped semiconductors.

It has been observed [14] that cleaning Si crystals by heating to 1500 K in vacuum always produces a thick degenerate p-type layer at the surface, irrespective of the bulk doping concentration or the type. A p-type accumulation layer will cause a positive electric field $\mathbf{E}=E\hat{x}$ which will hinder the diffusion of positrons to the surface. Thus the anomalously low value of $(D/\gamma)^{1/2}$ obtained by Mills [2] for Si prepared by heat treatment compared to that found for Ge can be explained by the inclusion of this surface electric field. The Ge crystal used was 20 Ω cm intrinsic material, which has a negligible surface electric field of $\lesssim 10^3$ V/cm [15, 16] at room temperature. The experimental result for Si can be explained by a tenfold reduction of $(D_{\rm eff}/\gamma)^{1/2}$ caused by an internal field of roughly 10^5 V/cm which corresponds [15, 16] to a p-type carrier concentration of $\sim 5\times 10^{19}/{\rm cm}^3$.

The use of externally applied electric fields in semiconductors [17] or those produced by surface preparation and doping provides exciting possibilities for improving slow positron convertors [18]. For example, cleaned, heavily doped n-type Si(111) surfaces might have both a negative positron work function [4] and a large negative surface electric field which would increase the effective diffusion of thermalized positrons to the surface, and thus the total yield of emitted slow positrons.

Since the fraction $L(a)$ of particles lost through the surface for a δ-function initial distribution is an exponential, see (6), the average of $L(a)$ with a stopping profile $P(a)$ is the Laplace transform of $P(a)$:

$$\bar{L}(\mathcal{E})=\int_0^\infty P(a)\,e^{-\xi a}da\,, \tag{10}$$

where $\xi=\sqrt{\gamma/D_{\rm eff}}$. In principle, we can therefore solve for $P(a)$ if we have a complete set of $\bar{L}(\xi)$ measurements as a function of ξ. This information can be obtained without any assumptions about the mean depth being linear in energy W if we vary ξ for example by changing the sample temperature T. In this case, we expect the diffusion constant to vary as $D\propto T^{-\sigma_1}$ with $\sigma_1=1/2$ for phonon-limited diffusion processes. More importantly, ξ will have a strong temperature dependence because the rate γ is the sum

of the bulk annihilation rate γ_b plus the trapping rate due to thermally activated vacancies [19]

$$\gamma = \gamma_b + D\nu\,e^{-E_v/kT}, \tag{11}$$

where ν is a constant proportional to the trapping crossection and E_v is the vacancy formation energy. We then have

$$\xi(T) = \sigma_0 T^{\sigma_1/2}(1+\sigma_2 T^{-\sigma_1} e^{-E_v/kT})^{1/2}. \tag{12}$$

Fitting $\bar{L}(\xi)$ data to (10) and (12) can therefore be expected to give information about the temperature dependence of D, vacancy activation energies and positron stopping profiles.

The data for determining $\bar{L}(\xi)$ would be, for instance, a set of measurements of the positronium yield $f(T, W)$ as a function of sample temperature T and positron incident energy W. A complication in making use of (10) is that the positronium formation fraction f_0 for the positrons which have reached the surface is temperature dependent [1]. This phenomenon is understood to be caused by the thermal desorption of positrons bound in the external "image" potential well at the sample surface [5]. Fortunately, it is found that positrons implanted into the solid at low energies (<100 eV) are sensitive primarily to the surface and do not become appreciably trapped in vacancies in the bulk. At high incident energies $f(T, W)$ is sensitive both to vacancies forming in the bulk and to the variation of f_0. If we normalize $f(T, W)$ to the low incident energy measurements $f(T, 0)$, we obtain $\bar{L}(T, W) = f(T, W)/f(T, 0)$, which should be a good approximation to the fraction of the incident particles diffusing to the surface.

In conclusion, positron diffusion can explain the incident energy dependence of the yield of positronium and slow positrons from surfaces being bombarded by slow positrons. Including the effects of internal electric fields allows us to explain an apparently anomalously low value [2] of the diffusion constant for positrons in Si. Finally, the formalism presented here may also provide the basis for measurements of positron trapping rates by vacancies in thin samples and near surfaces.

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References

1. K.F.Canter, A.P.Mills, Jr., S.Berko: Phys. Rev. Lett. **33**, 7 (1974)
2. A.P.Mills, Jr.: Phys. Rev. Lett. **41**, 1828 (1978)
3. K.G.Lynn: J. Phys. C **13**, L435 (1979)
4. A.P.Mills, Jr., P.M.Platzman, B.L.Brown: Phys. Rev. Lett. **41**, 1076 (1978)
5. A.P.Mills, Jr.: Solid State Commun. **31**, 623 (1979)
6. K.G.Lynn: Phys. Rev. Lett. **43**, 391, 803E (1979)
7. I.J.Rosenberg, A.H.Weiss, K.F.Canter: 5th Intern. Conf. on Positron Annihilation, Japan (April 1979); J. Vac. Sci. Tech. (to be published)
8. M.J.Fluss, K.G.Lynn: Private communication
9. K.G.Lynn, D.O.Welch: To be published
10. R.L.Bell: *Negative Electron Affinity Devices* (Clarendon Press, Oxford 1973)
11. J.Oliva: Ph. D. dissertation University of California, San Diego (1979) to be published
12. A.F.Makhov: Sov. Phys. Solid State **2**, 1934–1951 (1960)
13. A.P.Mills, Jr., L.N.Pfeiffer: Phys. Rev. Lett. **36**, 1389 (1976)
14. J.C.Rivière: *Solid State Surface Science*, Vol. 1, ed. by M.Green (Marcel Dekker, New York 1969) p. 179
15. A.S.Grove: *Physics and Technology of Semiconductor Devices* (Wiley, New York 1967)
16. R.M.Burger, R.P.Donovan: *Fundamentals of Silicon Integrated Device Technology*, Vol. 11 (Prentice Hall, Englewood Cliffs, NJ 1968)
17. T.T.Tsong: Surf. Sci. **81**, 28 (1979)
18. K.G.Lynn, B.T.A.McKee: Appl. Phys. **19**, 247 (1979)
19. I.K.MacKenzie, T.L.Khoo, A.B.McDonald, B.T.A.McKee: Phys. Rev. Lett. **19**, 946 (1967)