# Measurement of the Positron Surface-State Lifetime for Al

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The decay rate has been determined for positrons annihilating with electrons while localized in the image-induced potential well at the (110) surface of a clean well-annealed single crystal of Al at 300 K. The lifetime associated with positrons in this surface state was found to be 580 ± 10 psec. This value, which has never before been directly measured, is in disagreement with present theories. Changes in the lifetime spectra were also found from ion sputtering and from exposure of the surface to various amounts of oxygen.

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We report here the first measurement of the lifetime of thermalized positrons annihilating after localization on the surface of a single-crystal sample. A positron implanted into a well-annealed metal rapidly thermalizes and thereafter can annihilate with an electron, resulting predominantly in the emission of two gamma photons.[1] The rate of annihilation is determined by the overlap of the positron and electron wave functions and is enhanced as a result of electron-positron correlation (reducing the average positron lifetime), a situation which has been of much theoretical interest.[2,3] If open-volume lattice defects are created in most metals the positron lifetime increases with the size of the vacancy cluster. This effect has been widely utilized in the study of metal defects under various experimental conditions, including large defects such as voids (i.e., internal surfaces) produced by neutron or electron irradiation.[1] Theories which were developed to explain lifetime results in voids have led to predictions of annihilation rates on external metal surfaces. Since the early 1970's, a number of theoretical papers have reported calculations of positron surface-state lifetimes with values ranging from 300 to 500 psec.[4] The most detailed recent calculation by Nieminen and Puska[5] has predicted the surface lifetime ($\tau_{ss}$) to be $\approx 400$ psec for all surfaces of Al.

A knowledge of the annihilation rate of positrons residing at surfaces is desirable for several reasons. First, one can determine whether or not the theoretical models presently developed are adequate for predicting these decay rates. Secondly, one can provide many of the answers required to unravel the complex behavior of positrons at internal surfaces (voids) produced by irradiation. Lastly, these data should demonstrate whether or not positron surface-lifetime measurements will be useful as a probe of surface impurities or surface defects. Experimentally, the measurement of $\tau_{ss}$ has not been possible because of the large kinetic energy of positrons emitted from naturally occurring isotopes, which results in a very small fraction of positrons stopping near the surface. With the advent of variable-energy moderated positron beams coupled with ultrahigh vacuum surface physics systems these problems can now be overcome.[6,7]

In this Letter we report the first measurement of the surface-state lifetime. This measurement was performed on an electrostatic positron beam with use of a unique positron lifetime apparatus. The surface physics system used included both low-energy electron diffraction (LEED) and retarding-field Auger electron spectroscopy (AES) capabilities which were used to characterize the sample surface before and after each measurement.

Figure 1 shows a simplified schematic of the lifetime spectrometer. The incident postron beam ($10^5$ $\mathrm{sec}^{-1}$) was collimated and directed through a 45°

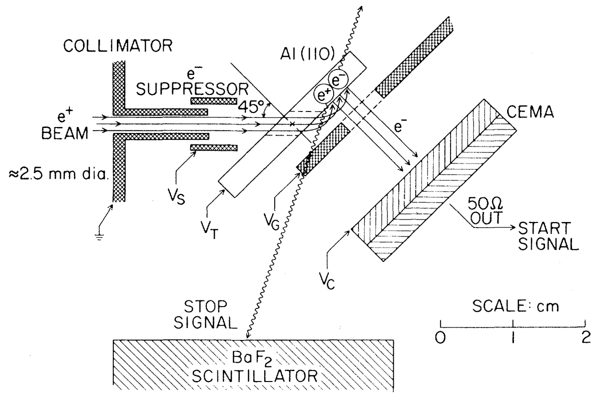

FIG. 1. Representative drawing of the lifetime apparatus. The biases on the various elements were $V_S$(suppressor) = $V_T$(target) = ground, $V_G$(grid holder) = 3.5 kV, $V_C$(CEMA face) = +300 V. The beam energy was 3 keV for most of the experiments.

hole in the Al(110) sample, and then deflected back onto the sample surface by a positive bias $V_G$ on a retarding grid. Most of the positrons hit the sample at angles of order 45° and those positrons ($< 10\%$) that were backscattered from the surface were biased back into the sample again by $V_G$. When a positron strikes a sample, secondary electrons are usually generated. These secondaries were accelerated by the bias $V_G$ through 90%-transmitting grids towards a channel electron multiplier array (CEMA) to provide the start signal for a time-to-amplitude converter. The grid holder was designed to prevent any electrons generated anywhere other than a controlled region of the sample surface from reaching the CEMA. The stop signal was produced by the annihilation photon which was detected with a high-efficiency $BaF_2$ scintillator coupled to an XP2020Q photomultiplier tube outside the vacuum system. The time-to-amplitude converter output was digitized by a pulse-height analyzer; coincidence count rates of order 20–30 $\sec^{-1}$ were obtained. Our sample was a 99.9999% pure Al(110) single crystal[8] which was spark cut and subsequently annealed, etched, and polished to a mirrorlike finish. The sample was cleaned *in situ* by sputtering with 3-keV $Ar^+$ ions and then annealed at 55 °C for $\approx \frac{1}{2}$ h and slowly cooled. In all cases the clean, annealed sample exhibited sharp LEED spots, and showed less than 1% of a monolayer of carbon and oxygen as determined by AES.

The lifetime data were analyzed with a nonlinear fitting routine where the timing resolution of the apparatus was appoximated by a function represented by a double-sided exponential convoluted with a Gaussian.[9] We have used a new result for the time dependence of the annihilation rate to account for the delay between the start signal when the positron strikes the surface and the time it takes to become localized in the surface state (or forms positronium at the surface). A one-dimensional diffusion model has been successfully employed by several workers[6, 10] to describe the motion of thermalized positrons which diffuse back to the surface before annihilation. (The average time required for thermalization is of the order of a few picoseconds and will be neglected here.) By combining the diffusion model with a simple trapping model,[1] one can obtain an expression for the decay rate as a function of time,[11] given by

$$n(t) = A_b \rho_b(t) \exp(-\kappa_b t) + \textstyle\sum_i \epsilon_i A_i \rho_i(t) \exp(-\kappa_i t), \qquad (1)$$

where $A_b = \kappa_b - \sum_i \epsilon_i A_i$; $A_i = \kappa_i \kappa_D / (\kappa_i + \kappa_D - \kappa_b)$;

$$\rho_b(t) = \exp(\kappa_D t) \operatorname{erfc}[(\kappa_D t)^{1/2}];$$

$$\rho_i(t) = 1 - \left\{ \frac{\kappa_b - \kappa_i}{\kappa_D} \right\}^{1/2} \operatorname{erf}\{[(\kappa_b - \kappa_i)t]^{1/2}\}.$$

Here we write $\kappa_b$ and $\kappa_i$ for the decay rates of freely diffusing bulk positrons and those associated with various surface-related components, $\epsilon_i$ for the branching ratios at the surface, and $\kappa_D \equiv D/x_0^2 = \kappa_b (E_0/E)^{3.2}$ for a rate representative of the diffusion process. [$E_0$ is an experimentally obtained parameter[10] equal to $\approx 3$ keV in Al, $D$ is the positron diffusion constant, and $x_0$ is the mean implantation distance for the exponential implantation profile that was used in obtaining Eq. (1).] It can be seen that Eq. (1) has the usual form of a sum of exponentials except that each exponential is modified by a function $\rho$ of time which takes into account the diffusion process. As $\kappa_D t \to \infty$ we find $\rho_b \to (\pi \kappa_D t)^{-1/2}$ and $\rho_i \to 1$ so that for times $t >> \kappa_D^{-1}$, the expression approaches a simple sum of exponentials. For Al at $\approx 2$ keV implantation energy, $\kappa_D^{-1} \approx 23$ psec.

Using Eq. (1) to fit our data resulted in lower values of $\chi^2$ than did a simple sum of exponentials. While the model can be extended to include more sophisticated expressions for the implantation profile, bulk defects, surface detrapping, and other effects,[11] these were not found to be significant in spectra for clean, annealed samples. In the case of sputtered or oxygen-exposed samples, these effects are more significant.

In the analysis of clean, well annealed Al we used three surface-associated components: the surface state, orthopositronium (*o*-Ps) formation, and parapositronium (*p*-Ps) formation. In the fit, we constrained $\tau_b = 163$ psec,[9] $E_0 = 3$ keV, $\tau_{o\text{-Ps}} = 142$ nsec, $\tau_{p\text{-Ps}} = 125$ psec, and $\epsilon_{o\text{-Ps}} = 3\epsilon_{p\text{-Ps}}$.[12] This last constraint is due to statistical weighting of the positronium spin states. The adjustable parameters in the fitting routine are $\tau_{ss}$ (for the surface state), $\epsilon_{ss}$, $\epsilon_{p\text{-Ps}}$, an overall scale factor, and a flat background. In addition, the resolution function which was convoluted with Eq. (1) has three free parameters, the full width at half maximum and the left- and right-hand exponential slopes.

The modified trapping model fit [Eq. (1)] and data are shown in Fig. 2 and the parameters deduced are listed in Table I for four runs on clean Al(110). Lifetime spectra were also taken after sputtering with 3-keV $Ar^+$ ions as well as after ex-

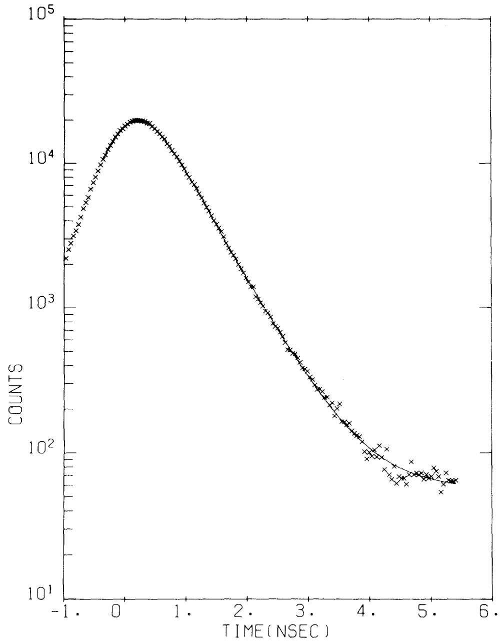

FIG. 2. A typical lifetime spectrum on clean Al(110) at 300 K shown with the normal component of the incident positron energy $\approx 2$ keV. The line represents the best fit of Eq. (1) to the data. The deduced fitting parameters are listed in Table I.

posures of 100, 500, and $5\times10^5$ L of $O_2$ (1 L $=10^{-6}$ Torr sec). In these cases the $\tau_{ss}$ lifetime was reduced to $\approx 400$ psec and another lifetime (650–700 psec) of $\approx 10\%$ intensity appeared in the sputtered sample while a lifetime of $\approx 1$ nsec appeared for large oxygen exposure. In all cases (i.e., clean, sputtered, and oxidized) a number of similar runs at various times during the experiment were made and the results were consistent.

TABLE I. The results obtained for four different runs on clean, annealed Al(110), giving an indication of the stability of the electronics and fitting routine. Different settings on the timing electronics were used for the last two sets in the table. Columns 3, 4, and 5 refer to the fitted parameters which represent the resolution function, where SL and SR are the left- and right-hand exponential slopes.

| $\tau_{ss}$ (psec) | $\epsilon_{ss}$ (%) | FWHM (psec) | SL (psec) | SR (psec) | $\chi^2/\nu$ | $10^{-5}\times$ counts |
|---|---|---|---|---|---|---|
| 579(2) | 63 | 604(7) | 461(4) | 250(2) | 160/200 | 6 |
| 581(4) | 71 | 600(4) | 580(2) | 236(1) | 180/200 | 6.7 |
| 584(2) | 66 | 628(12) | 468(11) | 245(5) | 160/200 | 7.8 |
| 578(2) | 68 | 628(11) | 523(6) | 233(4) | 220/200 | 4 |

The most significant problem to be dealt with was adequate knowledge of the actual timing resolution function. The resolution was thought to be dominated by trajectory effects such as positrons scattering off the sample surface, with intrinsic timing resolutions playing a lesser role. For example, in the worst case, a positron which undergoes a specular reflection from the surface will be returned by the grid bias in $\approx 250$ psec. Thus bouncing positrons ($<10\%$) could lead to a significant and rather complex structure in the resolution function. We were not able to measure the timing resolution directly; however, a number of checks were made for it in the data analysis. For example, fits were made with the resolution constrained to have longer exponential slopes or greater widths; in all cases, the goodness of fit was significantly worse and the $\tau_{ss}$ value was not changed significantly. Although these checks do not rule out problems due to the resolution, they make them less likely. It should also be noted in this regard that the data can be represented by a pure exponential slope for nearly two decades. It is quite difficult to devise a reasonable resolution function which gives a pure exponential result when convoluted with an exponential decay rate unless the resolution slopes are short compared with the exponent in the decay rate. Again this gives us confidence that our fitting procedure adequately deals with the resolution function in this case. Finally, one finds that shorter lifetimes ($\approx 400$ psec) appear after the sample has been sputtered or exposed to oxygen; since the resolution function should not change we have still further evidence that we are correctly identifying $\tau_{ss}$.

Other possible systematic errors were checked by varying the incident beam energy and the resolution function (i.e., by deliberately degrading the electronic timing characteristics). Lifetime spectra were taken every three hours to check if either electronic drifts occurred or whether impurities were changing the lifetime spectra during an experimental run. The fitting function was tested by artificially changing various parameters in the nonlinear program such as the background subtraction and the right- and left-hand sides of the resolution function as well as fitting the "usual" lifetime model[1] of a simple sum of exponentials instead of Eq. (1). In the latter case the goodness of fit was worse for all spectra, but no significant change was found for $\tau_{ss}$. Uncertainty due to these systematic effects adds to the statistical errors (Table I) in fitting our data to produce an overall error of ± 10 psec.

To suggest a possible resolution to this discrepancy between theory ($\tau_{ss} = 400$ psec) and experiment ($\tau_{ss} = 580 \pm 10$ psec), it is necessary to briefly outline the calculational procedure. The most recent calculation of the surface lifetime was done using the local-density approximation where screening is implicitly included.[5] Since only a single-particle potential (including the image potential) was used, one would expect that considerable error could be present in this potential. Moreover a locally homogeneous electron gas without external fields was assumed for the enhancement factor to deal with the correlation of the electron gas with the positron. With this approach the maximum lifetime that can be theoretically calculated is $\approx 500$ psec (i.e., the spin-averaged Ps decay rate). In actuality the surface dipole can create electric fields as high as $10^9$ V/cm, fields comparable in strength to those within a positronium atom itself. It is thus by no means unreasonable to expect considerably lower enhancement effects (i.e., longer lifetimes) for the positron in the surface region than those predicted by current theory.

In conclusion, we have measured the lifetime of positrons localized at the surface of an Al(110) crystal to be $\tau_{ss} = 580 \pm 10$ psec. This lifetime is significantly longer than any theoretical estimate published and it is suggested that the discrepancy is related to an oversimplification of the electron screening of the positron. A quantitative estimate of the correct enhancement factor and of the use of a fully self-consistent potential awaits further theoretical development.[13] (These results should also have impact on screening calculations of positive muons and protons at surfaces.)

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