Positronium Formation at Surfaces

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A beam of positrons is used to study positronium (Ps) formation at the surfaces of clean, single-crystal targets. The Ps formation probability changes with incident energy E as $(E/E_0+1)^{-1}$, with $E_0=915(30)$, 6000(150), and 2900(150) eV for Si, Ge, and Al at 300 K. Since E_0 is observed to be temperature dependent, it is argued that Ps is not being formed by backscattering from the surface; rather, the energetic positrons thermalize in the bulk and diffuse to the surface where about half of the positrons escape as free Ps at 300 K.

Ten years ago, Paulin and Ambrosino[1] reported that positronium (Ps) is formed efficiently when ~200-keV β-decay positrons are stopped in metal oxide powders. It is thought that the Ps forms within a powder grain, diffuses to the surface, and escapes into the voids between the grains.[2] The importance of surfaces in this connection became evident with the more recent discovery[3] that free Ps is formed with high efficiency when slow (~10 eV) positrons impinge upon solid targets in vacuum. The surprising observation was that metal targets formed Ps even more efficiently than metal oxide targets, Ps being forbidden to exist within a bulk metal.[4] Because of the unknown surface condition of the metal targets and the small penetration depth of the incident particles, this study left open two important questions concerning the Ps formation process: Is the Ps formation associated with the metal surface itself or must surface oxides or other contaminants be present? Furthermore, is Ps formation a surface backscattering phenomenon[5] possible only for externally incident low-energy positrons? In other words, does surface trapping[6] of thermalized positrons which reach the surface from within prevent Ps formation in spite of the expectation that Ps has a negative work function for most materials?[7]

The present study gives definitive answers to these two questions. Ps formation is indeed observed to be the dominant process for slow positrons incident upon single-crystal metal targets with submonolayer surface contimination. Moreover, the Ps formation is temperature dependent and persists for very high incident energies. This implies that positrons implanted into a metal thermalize and then diffuse to the surface where they can escape with high probability by the formation of free Ps. This fact has important implications for positron studies of void formation in metals.[8] The present measurements also provide a new way to estimate the positron diffusion constant in metals[9] and to observe the interaction of positrons with vacancies.[10]

The positronium formation probabilities are measured with an apparatus similar to that of Ref. 3, modified to make it compatible with surface studies. Monoenergetic positrons ($\Delta E<2$ eV) from a 200-mCi ^{58}Co source and slow positron converter are guided by a 30-cm-diam 150-G solenoid to a target located in an all-stainless-steel bakable vacuum chamber with base pressure 1.0×10^{-10} Torr measured at a point farthest from the pump. A manipulator is used to position the target for LEED (low-energy electron diffraction) and Auger analysis,[11] ion bombardment cleaning, and positron-annihilation measurements.

The annihilation of positrons is detected by a 3×3-in. NaI(Tl) scintillator located behind the target. The 0.5-cm full-width at half-maximum positron beam passes through a 2.5-cm aperture into a 10-cm-diam × ~8-cm-long space and strikes the (~2×2 cm^2) target surface at normal incidence. A multichannel analyzer is used to measure the counting rate in two regions of the NaI(Tl) energy spectrum: a "total"-count-rate region T with $70<E<588$ keV and a "photopeak" region P with $448<E<588$ keV.

Ps may be detected by studying the energy spectrum[12] of its annihilation photons because the $^3S_1$ state decays into 3γ's with a continuous energy distribution in the range 0 to $mc^2=511$ keV, whereas positrons which annihilate with an electron of a solid decay principally by $^1S_0$ overlap via 2γ's with energy mc^2. Assume that a fraction f of the positrons which annihilate in the target region form PS. Let T_f and P_f be the "total" and "photopeak" NaI(Tl) counting rates for a given number of positrons annihilating per second. It is evident that $T_f=fT_1+(1-f)T_0$ and $P_f=fP_1+(1-f)P_0$, where the subscripts 1 and 0 refer to $f=1$ and $f=0$, respectively. Forming the ratio $R_f=(T_f-P_f)/P_f$ to eliminate any dependence on the

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positron beam strength, we find[13]

$$f=[1+(R_1-R_f)(R_f-R_0)^{-1}(P_1/P_0)]^{-1}. \qquad (1)$$

To make use of Eq. (1), we need the three quantities R_0, R_1, and P_1/P_0. The no-Ps ($f=0$) values are obtained from measurements on a low-efficiency, Ps-producing target (mica) by extrapolating to infinite incident positron energy E as $1/E$. The 100% Ps ($f=1$) values are obtained from measurements on a very efficient Ps-producing target (Ge) at $E\approx 0$ extrapolated to high target temperature. Independent values of R_0, R_1, and P_1/P_0 (see Table I) were found for each sample.

Figures 1 and 2 show the Ps formation fraction f versus incident positron energy E for Ge(111), Si(111), and Al(100) targets. The incident positrons enter the target region at 19.5 or 80.2 eV and are accelerated by a negative bias on the target. The error of the f measurements is estimated to be $^{+5}_{-20}$% including the calibration uncertainties.[14] The data show the persistence of Ps formation at quite large incident positron energies. This suggests that positrons are eventually able to form Ps even if they first penetrate many atomic layers beneath the surface of the target. A model which naturally suggests itself is that the energetic positrons lose most of their energy by plasmon emission and subsequently diffuse to the surface, where they escape with an electron as free Ps.

Suppose particles with density $\varphi(x,t)$ are diffusing according to $D\nabla^2\varphi=\dot{\varphi}$ in one dimension. Let the particles have a lifetime τ in the material and escape with unit probability if they reach the surface boundary. The total loss of particles through the boundary is a fraction $N(a)=(a\sqrt{D\tau}+1)^{-1}$ of the original particles if the initial distribution is exponential with mean depth a. With the assumption that the mean depth is linear[15] in E, $a=AE$, and denoting by f_0 the positronium fraction at $E=0$, we have the prediction

$$f=f_0(E/E_0+1)^{-1}, \qquad (2)$$

where $E_0=\sqrt{D\tau}/A$.

The solid curves shown in Figs. 1 and 2 are the result of least-squares fitting this function to the

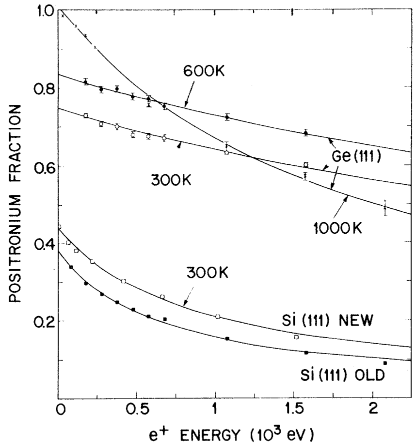

FIG. 1. Positronium formation fraction f versus incident energy E for various target surfaces. The Ge(111) surface showed a partially resolved eight-order LEED pattern. The surface contamination in monolayers was estimated by Auger analysis to be < 2.5% C and < 0.4% O. The "new" Si(111) target was cleaned by heating and showed a very clear 7×7 LEED pattern. The "old" Si surface is a repeat measurement after one week under vacuum. After two weeks under vacuum, the only contaminant detectable was C, 7% with < 0.2% O. The curves have the form of Eq. (2) and have been least-squares fitted to the data with the parameters given in Table I. Only errors due to counting statistics are included in the error bars.

TABLE I. List of target surfaces studied and the parameters f_0 and E_0 used to fit the data of Figs. 1 and 2 to curves of the form given by Eq. (2). χ^2/ν is the χ^2 per degree of freedom. The parameters R_1, R_0, and P_1/P_0 used in applying Eq. (1) are also given.

Target surface	T (K)	f_0 ($^{+5}_{-10}$%)	E_0 (eV)	χ^2/ν	R_1	R_0	P_1/P_0
Ge(111)	300	0.75	6000 ± 150	15.84/6	2.90	1.15	0.59
	600	0.84	6850 ± 270	3.18/6			
	1000	1.00	1965 ± 30	28.43/6			
Si(111) new	300	0.44	915 ± 30	12.97/6	4.35	1.00	0.39
Si(111) old	300	0.38	700 ± 20	20.67/9			
Al(100)	300	0.68	2860 ± 150	18.29/6	3.08	1.15	0.65
	500	0.83	2740 ± 100	37.02/9			

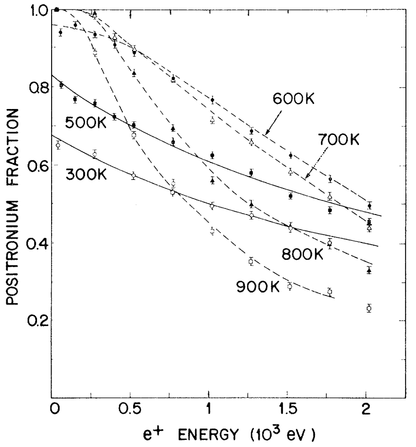

FIG. 2. Positronium formation fraction f versus incident positron energy E for an Al(100) target surface. The Al was cut from an ingot represented to be 99.9999% pure and to have a resistance ratio of 5600. The cleaned surface of the target showed a sharp (100) LEED pattern. The surface contamination in monolayers was estimated by Auger analysis to be < 3% C and < 0.5% O. The temperatures indicated are the temperatures of the target holder. Only the 300- and 500-K data could be fitted using Eq. (2). The dashed lines are drawn to connect data points at a constant temperature.

data. The fitting parameters are given in Table I. Equation (2) is evidently a remarkably good representation of the data. It is thus likely that the Ps formation occurs after implanted positrons diffuse to the surface of a clean target. Note, however, that the Ps yield at zero energy and the energy dependence of f both show a strong temperature dependence! This is very strong evidence that the diffusion process by which the positrons reach the surface and the Ps emission process both involve thermalized positrons. At high temperatures, Fig. 2 shows that the diffusion length in Al is shortened drastically, presumably because the positrons are being trapped by vacancies[10] at a rate comparable to the annihilation rate.

The Ps formation probability at low incident positron energies has a temperature dependence characteristic of an activated process for Ge, Si, Al, and other materials.[16,17] The clarification of the mechanism of this temperature dependence is presently under study.

At 300 K, Al, Si, and Ge are found to reemit 17%, 7%, and <1% of 1-keV incident positrons as slow positrons[17] with $E < 1$ eV. Since the targets in the present experiment were negatively biased, the reemitted slow positrons are partly converted to Ps and the 300-K Al and Si data overestimate by ~10% the Ps formation which would be seen if the slow positrons could escape. No such correction would be necessary for the Al data above 700 K or the Ge data at any temperature since there appears to be little slow positron emission in such cases.

We may estimate the depth of penetration of the incident energetic positrons for the case of Ge because the positron mobility μ_+ is known at low temperatures.[18] Scaling the diffusion constant $D_+ = \mu_+ kT/e$ as $T^{-1/2}$, we find a diffusion length $\sqrt{D\tau} = 1100$ Å at 300 K. From the constant E_0 in Table I, we then calculate a penetration depth $A = \sqrt{D\tau}/E_0 = 180$ Å/kV. For Si,[19] we estimate $\sqrt{D\tau} = 1900$ Å and $A = 2000$ Å/kV. The latter value seems too large and may indicate that D is really much smaller than estimated.

If we assume that the stopping of the incident positrons is not temperature dependent, the E_0 data of Table I show that the diffusion constant for positrons is not strongly temperature dependent in Ge between 300 and 600 K or in Al between 300 and 500 K. Assuming that the stopping length A is similar in Al and Ge implies that the diffusion constant in the single-crystal metal is about 0.1 cm^2/sec, a value which is 10 times greater than was found in measurements on various metal powders.[9]

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[14] The unsymmetric error estimate quoted allows for the possibility that some e^+ might not escape from the surface as Ps at high temperatures. The Ps formation was also measured in a separate experiment which used a Ge(Li) detector. The relative intensities of the background-subtracted 511-keV photopeaks were found to be 0.466(5), 0.764(7), and 1.00(1) for (1) a Ge(111) target at 1000 K, 32-eV e^+, (2) the same target but with 1490-eV e^+ incident, and (3) an unclean Al target at 300 K, extrapolated to high-energy e^+ as $1/E$. This results means that 53% of the annihilations were via 3γ for low-energy e^+ on Ge at 1000 K and that the Ps fraction is not less than $\frac{4}{3} \times 53\% = 71\%$. The photopeak for 32-eV e^+ on Ge at 1000 K was found to be red-shifted 100 ± 20 eV compared to the photopeak for 1490-eV e^+ on the same target. The shift is interpreted as a Doppler shift from $^1S_0$ Ps emitted from the target surface and receding from the detector as expected. The Ps energy is estimated to be about 1 eV. With such energies, it would not be unreasonable if one-quarter of the $^3S_1$ Ps annihilated via 2γ's because of wall collisions, thus accounting for the 53% 3γ yield at what appears to be $f = 98$.

[15] In the approximation that $dE/dx \propto 1/E$, the total path length S will be $S \propto \int_0^E E' \, dE' \propto E^2$. The mean penetration depth a will be less than S because the path is not a straight line. If the number N of collisions which significantly change the momentum direction is proportional to S, we then have $a \approx S/\sqrt{N} \propto E$.

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Azimuthal Anisotropy in Core-Level X-Ray Photoemission from $c(2\times2)$ Oxygen on Cu(001): Experiment and Single-Scattering Theory

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Azimuthal anisotropies in core-level x-ray photoemission from $c(2\times2)$O on Cu(001) have been found to show a strong dependence on polar emission angle. The anisotropies observed are $\Delta I/I_{\max} \lesssim 24\%$ for O 1*s* emission, and $\lesssim 41\%$ for Cu $2p_{3/2}$ and Cu $3p$ emission. A single-scattering theoretical model is found to describe well both the O and Cu data, and suggests that O is present in fourfold coordination sites for which the O atoms are coplanar with the Cu surface atoms.

Kono, Fadley, Hall, and Hussain (KFHH)[1] have recently reported the first observation of azimuthal anisotropies in deep core-level x-ray photoemission from adsorbed atoms, specifically $c(2\times2)$O on Cu(001), and qualitatively discussed the utility of a single-scattering theoretical model for interpreting such data. In the present study, a higher-resolution and much-more-detailed set of azimuthal scans for both O and Cu levels at various polar angles is considered. The experimental data are found to compare favorably with quantitative theoretical calculations involving a single-scattering model, and the adsorbate bonding geometry is determined.

The experimental procedure has been discussed in KFHH.[1] Unpolarized Al $K\alpha$ radiation (1487 eV) was used for excitation. The polar emission angle θ is measured with respect to the surface, and the azimuthal angle φ with respect to the [100] crystal axis. A 1200-L (1 L = 10^{-6} Torr sec) exposure of oxygen was used to produce the $c(2\times2)$ structure (as verified by low-energy electron diffraction). Azimuthal scans were made for both the substrate peaks Cu $2p_{3/2}$ ($E_{\text{kin}} = 551$ eV) and Cu $3p$ (1408 eV) and the adsorbate O 1*s* peak (951 eV). Data processing involved the two-step procedure of fourfold averaging via $I = I(\varphi) + I(\varphi + 90°) + I(\varphi + 180°) + I(\varphi + 270°)$ and a subtraction of the minimum intensity. The resulting "flower patterns" amplify anisotropy and minimize spurious sources of nonfourfold anisotropy,[1] as shown for O 1*s* in Fig. 1.

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