New Mechanism for Positronium Formation on a Silicon Surface

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Department of Physics and Astronomy, University of California, Riverside, CA 92521-0413, USA

We describe experiments in which positronium (Ps) is emitted from the surface of p-doped Si(100), following positron implantation. The observed emission rate is proportional to a Boltzmann factor, $\exp\{-E_A/kT\}$, which is dependent on the temperature T of the sample and a characteristic energy E_A=(0.253±0.004) eV. Surprisingly, however, the Ps emission energy has a constant value of ~ 0.16 eV, much greater than kT. This observation suggests the spontaneous emission of energetic Ps from a short-lived metastable state that becomes thermally accessible to available surface electrons once the positron is present. A likely candidate for this entity is an electron-positron state analogous to the surface exciton observed on p-Si(100) c(4×2) by Weinelt et al. [Phys. Rev. Lett. **92**, 126801 (2004)].

Since the creation of the first practical slow positron beams nearly four decades ago [1], the formation of positronium (Ps) at surfaces following the implantation of positrons into metals and semiconductors has been extensively studied [2, 3]. This can occur in two ways. (1) Ps may be formed directly if a positron picks up an electron from the conduction band as it is emitted into the vacuum with a range of kinetic energies from zero to a maximum that is largely unaffected by the sample temperature [4]. (2) For some materials positrons may become trapped in a surface state [5, 6] and then be thermally desorbed as Ps at a rate governed by the sample temperature via a material dependent activation energy and surface sticking coefficient [7]. Thermal Ps of this kind is emitted with a beam-Maxwell-Boltzmann velocity distribution [8, 9].

Here we describe experiments demonstrating that the p-Si(100) surface supports a new mechanism for Ps formation wherein nearly mono-energetic (E ~ 0.16 eV) Ps is emitted at a rate that depends on the sample temperature, in contrast to other known Ps formation processes. The apparatus used for this work has been described in detail elsewhere [10]. A positron accumulator provides pulses with approximately 20 million particles that are compressed in time to a width of ~ 1 ns and implanted into a Si target whose temperature may be varied from 300 to 1000K. All experiments were conducted in an axial magnetic field of 0.16 T. The laser systems used in this work are essentially the same as those described in ref [11], except for a modification that allows for automatic tuning of the dye laser wavelength.

The $10\times10\times0.34$ mm^3 target was cleaved from a p-Si(100) wafer [2.7 Ωcm at 300K, $(5.2\pm0.2)\times10^{15}$ Boron atoms cm^{-3}], etched in ~2% HF for ~1 minute to remove the surface oxide (as evidenced by the surface becoming hydrophobic), rinsed in distilled water, and evacuated in the target chamber within ~2 minutes. This preparation is known to produce a hydrogen-terminated surface [12] which can lead to a (2×1) dangling bond surface at 300K after the hydrogen has been desorbed by heating to 1000K [13]. While the vacuum system was baked at a temperature of ~ 200°C for 36 hours the sample was outgassed at 300°C, and then gradually heated to 1000K. During the heating process, the positronium formation fraction increased, presumably due to the desorption of hydrogen, with the surface eventually becoming stable under repeated thermal cycling from 300K to 1000K. Auger spectroscopy of similarly prepared samples shows surface contamination of ~ 5% of a monolayer of carbon and < 2% of oxygen.

The amount of Ps produced following positron implantation into the Si target was determined using the technique of single shot positron annihilation spectroscopy [14]. Lifetime spectra are analyzed to determine the delayed fraction, f_d, which is defined as the fraction of such spectra in the interval of 50 to 300 ns after the prompt peak [11]. The Ps yield measured in this way is shown in Fig.1(a) which has a constant non-Ps background signal of amplitude 4% subtracted. The solid line is a fitted Arrhenius thermal activation function, containing a single Boltzmann factor

$$f_d = f_0 + f_1 /[1+(\gamma_s / r_A)\exp\{E_A / kT\}]. \qquad (1)$$

Here γ_s is the surface positron annihilation rate (1.46 ns^{-1} [15]), r_A is a temperature independent effective attempt frequency for the process, and f_0 and $f_0+ f_1$ are the minimum and maximum Ps fractions respectively [7]. The fit yields an activation energy, E_A= 0.253 ± 0.004 eV. These data show that Ps is mostly produced via a thermally activated process, as has been observed for numerous surfaces [3], including n-Si(100) [6, 16]. The fit to the total Ps fraction at low densities and small positron implantation energy suggests there is a temperature invariant component (f_0) in addition to the thermally activated component. While this overall picture would seem to suggest that Ps emission from our Si sample is not qualitatively different from that of, say, an Al surface [17], in fact the observed Ps energy distribution demonstrates that this is not the case.
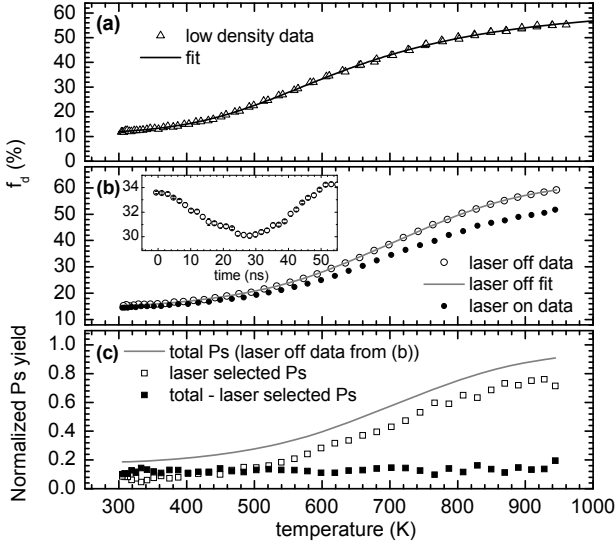
FIG.1. Ps yield as a function of temperature using a low density (unbunched) positron beam (a), and with a higher density bunched beam with and without a resonant 1S-2P laser (b). A decomposition of the total yield into various components is shown in (c), with the total Ps curve being proportional to the laser off fit of panel (b). The solid line in (a) is a fit to the data using Eq. 1. The inset in (b) shows a time of flight spectrum taken at 650 K. Errors bars are smaller than the symbols.

Our single shot lifetime spectra measure the total amount of Ps produced, regardless of its energy. However, it is possible to preferentially select the Ps energy range observed via the Ps time of flight (TOF) [8]. We do this via laser spectroscopy, using a 2 mm diameter laser beam running parallel to and 5 mm in front of the Si surface. Ps is excited to the 2P state with ~1 mJ pulses of UV light (λ ~243 nm), and the excited state Ps is subsequently photoionized by a ~ 40 mJ pulse at 532 nm. Liberated positrons annihilate upon returning to the Si target, changing the measured value of f_d as shown in Fig.1(b) [11]. Changing the delay between the positron and laser pulses results in a TOF measurement, as shown in the inset to Fig.1(b). The laser-on data in Fig.1(b) were taken with the laser pulses delayed with respect to the positron pulse by 25 ns, which preferentially selects Ps with a kinetic energy component perpendicular to the Si surface of ~ 200 meV.

The laser on and laser off data of Fig.1(b) are decomposed into two components in Fig.1(c) as follows. First the two sets of data are normalized to unit Ps yield at high temperatures with the laser off: $Y_d^{on(off)}(T) = f_d^{on(off)}(T)/f_d^{off}(\infty)$. Then, using the fitted curve for $Y_d^{off}(T)$ (smooth curve in Fig.1c) and the measured values for $Y_d^{on}(T)$, we calculate the normalized difference $\Delta Y_d(T) = N[Y_d^{on}(T) - Y_d^{off}(T)]$ (open symbols in Fig.1c), with the normalization constant N=7.5, ideally equal to one over the efficiency for laser detection of fast Ps, chosen so that the remaining component $Y_B(T) = Y_d^{off}(T) - \Delta Y_d(T)$ is constant $Y_B(T) \approx 0.13$ (filled

symbols in Fig.1c). Since $\Delta Y_d(T)$ has the same shape as a constant plus $f_d^{off}(T)$, it is not inconsistent with the data to estimate that the total Ps yield (solid line in Fig.1c) is composed of three components: A, thermally activated 0.2 eV Ps, 81% (maximum), B, temperature invariant 0.2 eV Ps, 6% and C, temperature invariant Ps of kinetic energy significantly different from 0.2 eV, 13%. To learn more about these three components and their origin we need more precise information about the Ps energy distributions.

Although in principle TOF spectra can yield the Ps energy, the resolution of this measurement is very low, largely due to the ~2 mm spot size of the laser beam and the fact that the 1S-2P transition is saturated, so that Ps may be detected out into the wings of the beam profile. A more accurate determination of the Ps energy distribution was obtained using the Doppler profile of the 1S-2P transition. When the sample surface is parallel to the laser beam (see inset to Fig.2a) the component of the Ps velocity distribution parallel to the Si surface may be determined from the linewidth [18]. With the sample rotated by $(68\pm2)^o$, such that Ps is emitted almost in the direction of the incoming lasers (see inset to Fig.2b), there will be a shift in the line center that is mostly due to the component of the Ps velocity perpendicular to the Si surface [19]. Line shapes measured in this way are shown in Fig. 2. The measurements are plotted as peak-normalized amplitude versus $\Delta\lambda$, the laser wavelength relative to the measured λ_0 = 243.01 nm 1S-2P line center. The distribution of velocities parallel to the surface (Fig.2a) is approximately a Gaussian symmetric about λ_0, whereas the distribution of velocities perpendicular to the surface (Fig.2b) exhibits two peaks, shifted by equal amounts to either side of λ_0. The shift to higher wavelengths is due to the interaction of Ps with the incoming beam, whereas the shift to lower wavelengths is due to Ps interactions with uv laser light that is reflected from the Si target.

Figure 2 (c) shows the mean energies $\langle E \rangle$ versus T, determined by computing the mean square wavelength deviation [20] and the relation $\langle E \rangle = m_e c^2 \langle \Delta\lambda^2 \rangle / \lambda_0^2$ for the component of energy associated with motion parallel to the surface (open symbols), and the identical expression times $1/\sin^2\theta = 1.163$ for the perpendicular energy component (filled symbols). The perpendicular and parallel energies for $T > 550$K are nearly constant with average values $\langle E_\perp \rangle = 0.160 \pm 0.008$ eV, and $\langle E_\parallel \rangle = 0.080 \pm 0.005$ eV. As the thermally activated Ps dominates at high temperature, these energies are identified as being characteristic of component A of the Ps yield.

Calculating the mean Ps energies in this way does not require any assumptions about the velocity distribution of the emitted Ps which, as we do not have a thermal distribution, is not necessarily known. At lower sample temperatures the energies appear to increase significantly. Examination of the spectra in Fig.2 (a) and (b) reveals the presence of a low

amplitude component with perhaps double the velocities of the main component, suggesting identification of this component with the temperature invariant component C of Fig.1c. As this Ps makes up around 2/3 of the total signal at low temperature its contribution to the total mean energy yields a higher value than at higher temperatures. These data show conclusively that the observed Ps emitted is not itself thermal, even though it is produced by a thermally activated process.
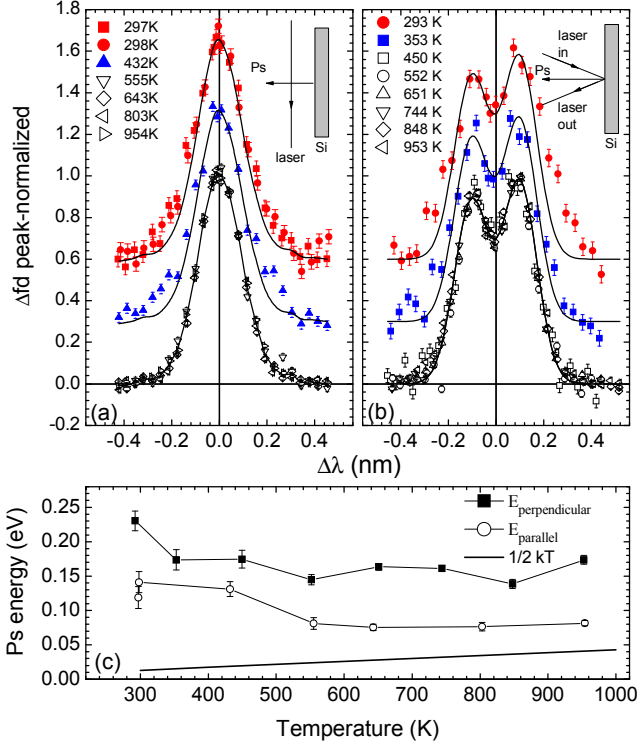

FIG.2. (color online) 1S-2P line shapes measured for different sample temperatures at $\theta=0°$ (a) and $\theta=68°$ (b). The curve in (a) is a spline fit to the average of the high temperature measurements (open symbols). The same curve is superimposed on top of the lower temperature measurements (filled symbols) to emphasize the presence of a low amplitude component having a full width at half maximum (fwhm) that is about twice that of the main component. In (b) the curve is a two-Gaussian fit to the high temperature data. The Ps energies derived from (a) & (b) are shown in (c), and the solid line in this figure is $kT/2$.

We explain this curious behaviour assuming our Si surface approximates the well-known electronic structure of p-Si(100) (2×1). This surface is terminated by buckled chains of pi-bonded pairs of Si atoms [21], from each of which projects a dangling single electron state, either filled or empty, that form a pair of surface bands. At 300K, we have a band of normally filled dangling bond states, D_{up}, the Γ-point of which is at an energy E_{up}=-0.15±0.05 eV below the valence band maximum (VBM) [22]. The VBM energy relative to the vacuum is the ionization potential, χ_-=(5.40±0.03) eV [22]. There is also a band of normally empty dangling bond states, D_{down}, for which the Γ-point is E_{down}= 0.61±0.05 eV above the VBM at 300K. The Fermi level for our sample is

E_F=0.21±0.02 eV above the VBM at 300K, increasing to 0.48 eV at 600K. The conduction band minimum (CBM) or energy gap is E_{gap}=1.128±0.005 eV above the VBM at 300K.

Our observations suggest that some state Z is being populated according to a Boltzmann factor and that Ps is being emitted with about 0.16 eV of kinetic energy from this state. This state cannot be purely electronic, else it could not have the simple Boltzmann-like thermal dependence observed in Fig.1a, due to the fact that the Fermi energy is a strong function of the temperature. On the other hand, if Z cannot exist without a positron, a Boltzmann factor referenced to the Fermi level does not apply because it does not take into account the dynamics of populating this state after the positron lands on the surface. We propose that Z is a positronic surface exciton, PsX, analogous to the [D_{up} hole + D_{down} electron] surface exciton with binding energy (0.13±0.05) eV which is found on p-Si(100) c(4x2) [23]. The direct population of PsX from a thermal excitation of the surface positron in combination with one of the D_{up} electrons flipping to a D_{down} state in the Coulomb field of the positron would give a population proportional to $\exp\{-E_a/kT\}$ after a time of the order of the positron surface state lifetime, as required to explain the thermally activated component (A) of the Ps yield. Our measurement of E_a=0.25 eV implies a PsX binding energy relative to a free D_{down} electron and a surface positron $E_b = E_{down} - E_{up} - E_a$ = 0.51 eV. The K_{Ps} = 0.16 eV emission energy from spontaneous desorption of the PsX then implies a surface positron binding energy $E_S = \frac{1}{2}R_\infty - \chi_- - K_{Ps} + E_{up} + E_a = 1.34 \pm 0.05\,\text{eV}$, to be compared with E_S=2.06 eV, calculated by Fazleev et al. [15].

The temperature invariant component B, with the same Ps kinetic energy as A, may be explained if there is a small probability of forming PsX through the interaction of the surface positron with the electron-hole plasma created by the initial positron implantation.

Finally, the temperature invariant Ps component C with kinetic energies of order 0.6 eV may be explained by a bulk positron picking up a valence band electron just beneath the surface to form Ps with a maximum kinetic energy $K_{Direct} = \frac{1}{2}R_\infty - \chi_- - \phi_+ = 0.6\,\text{eV}$, which implies that the positron work function of our p-Si sample is $\phi_+ = (0.8 \pm 0.2)\,\text{eV}$, where the error estimate reflects our uncertainty in the energy of component C. The relative energy levels discussed above are shown schematically in Fig. 3.

This model suggests several possibilities for future work; the Ps formation mechanism should be quite different for n-Si(100), for which the D_{down} band would be filled. The hydrogen terminated p-Si(100) surface lacks dangling bonds and might emit almost no Ps, as suggested by our preliminary results obtained while first heating the sample. Experiments with more perfect surfaces [24] at low temperatures might show that the Ps is really monoenergetic, and emitted perpendicular to the surface. The suggestion that component B is related to the formation of electron-hole pairs is supported

by experiments currently underway which show an increased Ps yield due to laser-produced electron-hole plasmas.
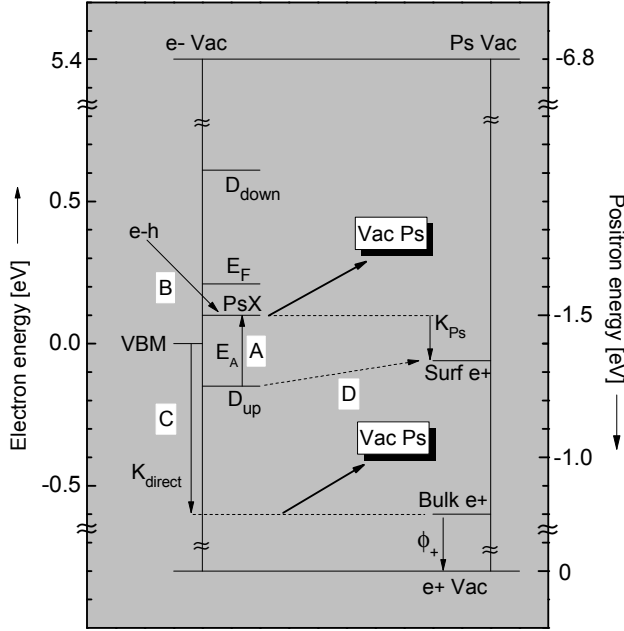

FIG.3. Schematic of electron and positron energy levels. The observed processes A, B, and C described in the text are indicated, along with another (unobserved) possibility, D, which is the thermal desorption of Ps with electrons from the D_{up} band. Here e-h refers to electron hole pairs created by the incident positron beam that directly populate the PsX state. The electron and positron energy scales have opposite senses so that the kinetic energy of Ps formed from a given pair of electron and positron levels is equal to the vertical separation of the two levels. The 0 eV electron reference level is the valence band maximum (VBM). The 0 eV positron reference level is that of a free positron in vacuum with zero kinetic energy. The electron vacuum level is 5.4 eV above the VBM and coincides with the -6.8 eV positron level corresponding to vacuum Ps at rest.

To summarize, we have observed a new mechanism for Ps emission from a p-Si(100) surface that appears to be mediated by a surface positronic exciton state. This level exists only when a surface positron is present, in which case it may be thermally populated by surface electrons. Ps emitted in this way has an energy of ~ 0.16 eV, regardless of the sample temperature.

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[20] The mean square wavelength deviation is defined as

$$\left\langle \Delta\lambda^2 \right\rangle = \sum_i \Delta\lambda_i^2 y_i e_i^{-2} / \sum_i y_i e_i^{-2} \pm \sqrt{\sum_i \Delta\lambda_i^4 / \sum_i y_i e_i^{-2}}$$,where y_i refers to

the peak-normalized amplitude and $\pm e_i$ are the error estimates.
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