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Positron Surface States on Clean and Oxidized Al and in Surface Vacancies

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This Letter reports on the first discrete-lattice calculation of positron surface states on the surfaces of Al. The authors reproduce the observed values and anisotropy of the binding energies on clean surfaces, and predict the surface-state lifetimes. The temperature-independent lateral diffusion constant is calculated. Monovacancies on surfaces are predicted not to trap positrons. The effect of ordered chemisorbed monolayers of oxygen is investigated: Oxidation makes the surface state unstable with respect to positronium emission.

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Intense, monoenergetic beams of slow (100 eV to 10 kev) positrons are emerging as a potentially powerful surface probe.[1] The momentum and lifetime spectroscopies of positrons interacting with solid surfaces convey useful information about both the atomic and the electronic structure. One particularly interesting facet of the positron-surface interaction is the image-induced surface state,[2] which has been the subject of extensive recent research, both experimental[3,4] and theoretical.[5]

In this Letter we report on the results of the first atomistic, discrete-lattice calculations of positron surface-state properties on the low-index surfaces of Al.

We have developed a general-purpose computational scheme[6] for positron states and their annihilation characteristics. The main steps are (i) construction of the positron potential, (ii) full *three-dimensional* solution (with proper boundary conditions) of the positron Schrödinger equation using numerical relaxation techniques, and (iii) calculation of the annihilation rates using the electron and positron states as input. In the present application, we construct the electron density and Coulomb potential by superimposing free atoms.[7] The correlation potential $V_{\rm corr}(\vec{r})$ to the metal side of the image plane is obtained from the local-density approximation.[8]

On the vacuum side of the surface, we use a simple expression for the image interaction. Along a fixed reference line normal to the surface,

$$V_{\rm corr}(\vec{r}) = -[4(z-z_0)]^{-1}, \qquad (1)$$

where z is the perpendicular coordinate, and z_0 defines the effective image-plane position. Furthermore, the image potential is constructed to have the same constant-value surfaces (corrugations) as the electron density, i.e., for any point $\vec{r}$ [electron density $n(\vec{r})$], it has the value equal to the one which corresponds to the density $n(\vec{r})$ on the reference line. The constant z_0 has been chosen to be 0.75 Å ($z = 0$ defines the nominal surface plane half an interlayer spacing outside the outermost atom layer) along a reference line on top of a (100)-surface atom. This value, which is close to that estimated from jellium calculations,[9] reproduces well the observed binding energies on clean surfaces. As first pointed out by Hodges and Stott,[2] the classical expression (1) is unphysical near $z = z_0$; a natural cutoff to $V_{\rm corr}$ is the positronium binding energy of −6.8 eV, which we also impose. This "corrugated-mirror" model of Eq. (1) is an approximation to the rather complicated dynamic and nonlocal image interaction.[5] However, by an appropriate choice of the image surface one can obtain a

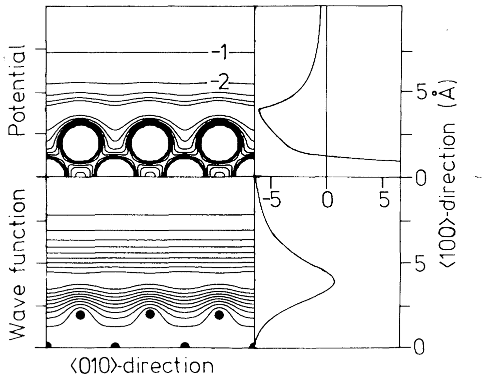

FIG. 1. Upper and lower panels: contour plots on Al(100) surfaces of the positron potential and wave function, respectively. The corrugated-mirror model is used. The black dots denote the positions of the atoms in the plane of the figure. The contour spacing in the lower panel is $\frac{1}{10}$ of the maximum value. Right-hand sections: cuts perpendicular to the surface.

good description of the clean-surface properties and then predict the effects of surface defects and adsorbates. For comparison, we have also carried out the calculations by using a "smooth-mirror" model, where z_0 is kept constant ($z_0 = 0.65$ Å).

Figure 1 shows the calculated positron surface state ψ_+ on Al(100), and the clean-surface results have been collated in Table I. The activation energy E_a for positronium desorption[3] from the surface is

$$E_a = E_b + \varphi_- - 6.8 \text{ eV}, \tag{2}$$

where E_b is the surface-state binding energy (with respect to vacuum) and φ_- the electron work function.[10] The agreement of the calculated E_a with experiment is encouraging. The surface-state lifetime τ is calculated from the local-density expression[8]

$$\tau^{-1} = \int d^3r\, |\psi_+(\vec{r})|^2 \Gamma(n(\vec{r})), \tag{3}$$

where $\Gamma(n)$ is the annihilation rate[8] in an electron system of density n. The results for E_a and τ are fairly similar in both the corrugated- and smooth-mirror models. For all the surfaces, $\tau \approx 400$ psec is predicted, clearly distinguishable from the bulk positron lifetime of 166 psec.

The positron state is extended on an ideal surface, and its mobility is determined by acoustic phonon and impurity scattering. Estimates for the phonon contribution can be obtained by using the deformation-potential model.[11] We have calculated the deformation-potential constants $\epsilon_d^{\parallel}$ and $\epsilon_d^{\perp}$ for dilatations parallel and perpendicular to the surface, respectively. The latter is found to be very small, indicating that the positron motion does not couple to phonons in this direction. Including the longitudinal surface phonons only, one obtains the scattering rate

$$\dot{n}_{\text{ph}} = m_{\parallel}(\epsilon_d^{\parallel})^2 k_B T/\hbar^3 \rho_A \langle c^2 \rangle, \tag{4}$$

where $m_{\parallel}$ is the positron effective mass, ρ_A the Al areal mass density, and c the average surface sound velocity. With use of the Einstein relation $D_+ = k_B T/m_{\parallel}\dot{n}$, Eq. (4) leads to a *temperature-independent* diffusion constant, in contrast to bulk behavior. The calculated values[12] of $\epsilon_d^{\parallel}$ and D_+ are also given in Table I. All the values of D_+ are larger than the room-temperature value[13] in bulk Al.

The impurity scattering rate is

$$\dot{n}_{\text{imp}} = n_i A_{\text{cell}} (\Delta V)^2 m_{\parallel}/2\pi\hbar^3, \tag{5}$$

TABLE I. Positron surface-state properties on clean Al surfaces. E_b is the binding energy, φ_- the electron work function, E_a the positronium desorption energy, τ the surface-state lifetime, $\epsilon_d^{\parallel}$ the surface deformation-potential constant, and D_+ the surface diffusion constant. The upper entries correspond to the corrugated-mirror model and the lower ones to the smooth-mirror model. All energies are in electronvolts.

	E_b	φ_- (Ref. 10)	E_a	E_a (expt.)	τ (psec)	$\epsilon_d^{\parallel}$	D_+ (cm^2/sec)
Al(100)	2.87	4.41	0.48	0.64[a]	397	2.7	1.2
	2.88		0.49	0.49[b]	396	1.3	5.0
Al(110)	2.95	4.28	0.43	0.40[a]	398	2.1	1.4
	2.85		0.33		394	1.3	3.6
Al(111)	2.84	4.24	0.28	0.34[a]	397	2.6	1.4
	2.99		0.43	0.41[b]	400	0.8	15.2

[a]Ref. 1. [b]Ref. 4.

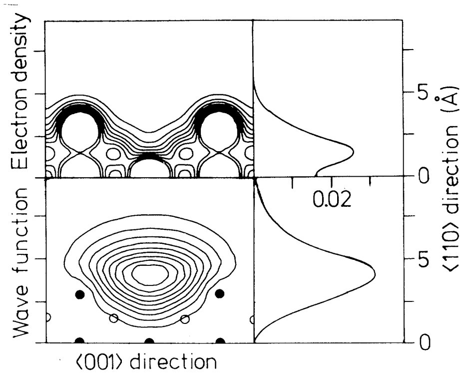

FIG. 2. The electron density and positron wave function in an Al(110) surface vacancy. The smooth-mirror model is used. See also the caption of Fig. 1; the open circles denote neighboring atoms not in the plane of the figure. The wave-function cut is taken through the center of the vacancy.

where n_i is the impurity concentration, A_{cell} the surface unit cell area, and ΔV the average potential difference between a host and impurity cell. Comparing Eqs. (4) and (5), we find that for Al impurity scattering starts to dominate below the temperature

$$T_C \cong (210\text{ K}) \times (\Delta V/\epsilon_a^{\parallel})^2 \times n_i(\text{at.\%}). \qquad (6)$$

Since $\Delta V/\epsilon_a^{\parallel}$ can be substantially larger than unity,[14] we conclude that impurity scattering is much more important than in the bulk, where usually $\Delta V/\epsilon_a < 1$.

Trapping of positrons in lattice vacancies is an important phenomenon in bulk defect studies.[15] We have searched for positron surface states *localized* at surface monovacancies in Al. Such a state is stable if it corresponds to an energy eigenvalue lower than in the extended state. In the corrugated-mirror model, *no* vacancy-trapped states exist on Al surfaces. In the smooth-mirror model, a stable surface vacancy state exists on Al(110), but *not* on Al (100) or Al(111). Figure 2 displays a positron surface state trapped at a monovacancy on Al(110). The binding energy to the surface vacancy is calculated to be only 0.4 eV and the lifetime is predicted to be 410 psec, just 16 psec longer than in the extended state. We conclude that monovacancies play little or no role for positrons on Al surfaces.

We have also considered the effect of ordered chemisorbed oxygen monolayers on the positron surface states. On Al(100) the oxygen position is chosen to be the fourfold hollow site, with oxygen atoms within the outermost Al plane.[16] The

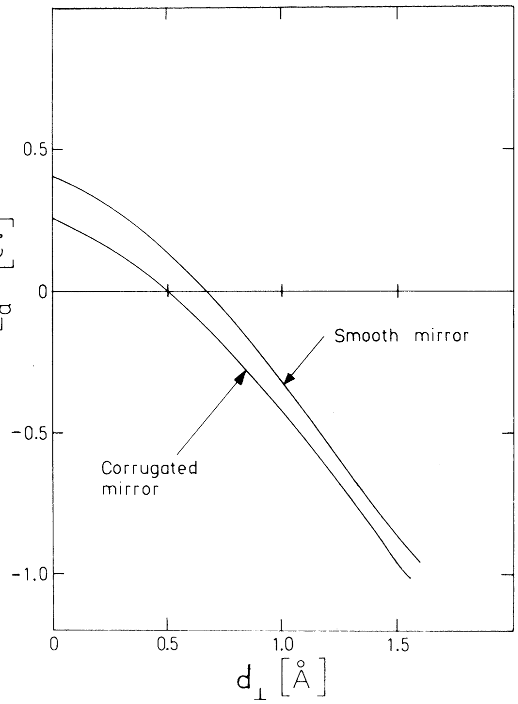

FIG. 3. The positronium desorption energy E_a for Al(111) surfaces covered with an ordered oxygen overlayer, with atoms at the threefold fcc stacking sites, as a function of the distance $d_\perp$ between the overlayer and the outermost Al plane.

charge density and Coulomb potential are again obtained from atomic superposition. In this case oxygen lowers the binding energy E_b only by less than 0.1 eV, but since the electron work function is lowered[17] by 0.6 eV, oxidation drives the positron surface state unstable with respect to positronium emission ($E_a < 0$). A different mechanism operates on Al(111). The electron work function hardly changes under oxidation.[17] We take the oxygen atoms to lie at the threefold fcc stacking sites, and calculate the binding energy as a function of the oxygen distance $d_\perp$ from the outermost Al plane. The image plane is kept in the clean-surface position. The results are shown in Fig. 3. The surface state becomes unstable at separations $d_\perp \geq 0.6$ Å. Since oxidation near monolayer coverages {exposures of around 500 L of O_2 [1 langmuir (L) = 10^{-6} Torr sec]} is known[4,18] to destroy the positronium thermal desorption on Al(111), we conclude that the Al-O distance has to be at least as large as this. This is consistent with both recent experiments[19] and *ab initio* calculations.[20]

In summary, we (i) calculate face-dependent binding energies and lifetimes for positron surface states, (ii) find that lateral diffusion constants on clean surfaces are temperature independent and enhanced over the bulk values, (iii) predict that vacancy trapping is not an important mechanism, and (iv) investigate the effects of oxygen overlayers. Positron surface-state spectroscopy, as gauged via positronium desorption and future lifetime studies,[21] is a useful surface tool. We show that its sensitivity is in principle high enough so that, in conjunction with a detailed calculational procedure, the observed parameter values can be correlated with atomistic surface information.

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