Nieminen, R. M.; Puska, M. J.

Positron surface states on clean and oxidized Al and in surface vacancies

Published in: Physical Review Letters

DOI: 10.1103/PhysRevLett.50.281

Published: 24/01/1983

Please cite the original version:
Positron Surface States on Clean and Oxidized Al and in Surface Vacancies

R. M. Nieminen

Department of Physics, University of Jyväskylä, 40100 Jyväskylä, Finland

and

M. J. Puska

Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland

(Received 30 August 1982)

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.

PACS numbers: 71.60.+g, 68.20.+t

Intense, monoenergetic beams of slow (100 eV to 10 keV) positrons are emerging as a potentially powerful surface probe. 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, which has been the subject of extensive recent research, both experimental and theoretical.

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 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. The correlation potential $V_{\text{corr}}(\mathbf{r})$ to the metal side of the image plane is obtained from the local-density approximation.

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,

$$V_{\text{corr}}(\mathbf{r}) = -[4(z - z_0)]^{1/4},$$

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 $\mathbf{r}$ [electron density $n(\mathbf{r})$], it has the value equal to the one which corresponds to the density $n(\mathbf{r})$ 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, reproduces well the observed binding energies on clean surfaces. As first pointed out by Hodges and Stott, the classical expression (1) is unphysical near $z = z_0$, a natural cutoff to $V_{\text{corr}}$, 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. However, by an appropriate choice of the image surface one can obtain a...
The 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 \( \varepsilon_0 \) is kept constant (\( \varepsilon_0 = 0.65 \text{ Å} \)).

Figure 1 shows the calculated positron surface state \( \psi_\alpha \) on Al(100), and the clean-surface results have been collated in Table I. The activation energy \( E_a \) for positronium desorption\(^a\) from the surface is

\[
E_a = E_b + \psi_\alpha - 6.8 \text{ eV},
\]

where \( E_b \) is the surface-state binding energy (with respect to vacuum) and \( \psi_\alpha \) the electron work function.\(^{10} \) The agreement of the calculated \( E_a \) with experiment is encouraging. The surface-state lifetime \( \tau \) is calculated from the local-density expression\(^a\)

\[
\tau^{-1} = \int d^3r |\psi_\alpha(r)|^2 \Gamma(n(r)),
\]

where \( \Gamma(n) \) is the annihilation rate\(^b\) in an electron system of density \( n \). The results for \( E_a \) and \( \tau \) are fairly similar in both the corrugated- and smooth-mirror models. For all the surfaces, \( \tau \approx 400 \text{ psec} \) 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 \( \epsilon_d \) 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

\[
\hat{n}_p = m_p |\epsilon_d^\parallel|^2 k_B T / \hbar^3 \rho_A (c^2),
\]

where \( m_p \) is the positron effective mass, \( \rho_A \) the Al areal mass density, and \( c \) the average surface sound velocity. With use of the Einstein relation

\[
D = k_B T / m_p \hat{n}_p,
\]

Eq. (4) leads to a temperature-independent diffusion constant, in contrast to bulk behavior. The calculated values\(^{12} \) of \( \epsilon_d \) 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

\[
\hat{n}_\text{imp} = n_i A_{\text{col}} (\Delta V)^2 m_p / 2 \pi \hbar^2,
\]

where

<table>
<thead>
<tr>
<th>( A_{\text{col}} )</th>
<th>( \Delta V )</th>
<th>( n_i )</th>
<th>( m_p )</th>
<th>( \hbar )</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm(^{-2})</td>
<td>V</td>
<td>cm(^{-3})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table I. Positron surface-state properties on clean Al surfaces. \( E_b \) is the binding energy, \( \psi_\alpha \) the electron work function, \( E_a \) the positronium desorption energy, \( \tau \) the surface-state lifetime, \( \epsilon_d \) 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.
where \( n_i \) is the impurity concentration, \( A_{\text{cell}} \) the surface unit cell area, and \( \Delta V \) 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

\[
T_c = (210 \, \text{K}) \times (\Delta V/\epsilon_d)^2 \times n_i (\text{at. \%}).
\]

(6)

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

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 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 \( (E_b < 0) \). 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 \( d_1 \) 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 \( d_1 = 0.6 \, \text{Å} \). Since oxidation near monolayer coverages \{exposures of around 500 L of O\(_2\) \[1 \text{langmuir} (L) = 10^{-6} \text{Torr sec}\]\} 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 \textit{ab initio} calculations.\(^{20} \)

In summary, we (i) calculate face-dependent binding energies and lifetimes for positron sur-
face states, (ii) find that lateral diffusion const-
stants on clean surfaces are temperature inde-
pendent 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 spec-
troscopy, as gauged via positronium desorption
and future lifetime studies, 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.

1For a review, see A. P. Mills, Jr., in Proceedings
of the International School of Physics “Enrico Fermi,”
Course LXXXIII, Varenna, Italy, 1981, edited by
W. Brandt and A. Dupasquier (to be published).
12, 1153 (1973).
3K. G. Lynn, Phys. Rev. Lett. 43, 391 (1979); A. P.
Mills, Jr., Solid State Commun. 31, 623 (1979); C. A.
Murray and A. P. Mills, Jr., Solid State Commun. 34,
789 (1980).
4K. G. Lynn, Phys. Rev. Lett. 44, 1330 (1980), and
in Ref. 1; K. G. Lynn and H. Lütz, Phys. Rev. B 22,
4143 (1980).
18, 2568 (1978); N. Barberan and P. M. Echenique,
14, 3975, 4951 (1981), and to be published.
6M. J. Puska and R. M. Nieminen, to be published.
7Comparison with self-consistent calculations [K. Med-
nick and L. Kleinman, Phys. Rev. B 22, 5678 (1980);
C. S. Wang, A. Freeman, H. Kraukaufer, and M. Post-
ernak, Phys. Rev. B 22, 1655 (1981)] reveals only rela-
tively minor differences, which are of lesser impor-
tance in the present context.
8M. Manninen, R. Nieminen, P. Hautojärvi, and
J. Arponen, Phys. Rev. B 12, 4612 (1975); J. Arponen
9N. D. Lang and W. Kohn, Phys. Rev. B 7, 3541
(1973).
Springer Tracts in Modern Physics Vol. 85 (Springer,
11J. Bardeen and W. Shockley, Phys. Rev. 80, 72
(1950).
12We calculate \( \epsilon_q = V \partial E_q / \partial q \) numerically by in-
creasing the surface unit cell size by a few percent. We
use the effective mass \( m_1 \approx 1.2 m_0 \). This arises solely
from metallic screening; we estimate the band contribu-
tion by the method of P. Kubica and M. J. Stott, J.
Phys. F 4, 1669 (1974), to be very close to unity.
Furthermore, we use the average surface sound veloc-
ity \( c \) \( \approx 6.4 \times 10^5 \) cm/sec.
13A. P. Mills, Jr., and R. J. Wilson, Phys. Rev. A
26, 496 (1982); B. Bergersen, E. Pajanne, P. Kubica,
15See, e.g., Positrons in Solids, edited by P. Hauto-
Järvi, Topics in Current Physics Vol. 12 (Springer,
16S. Flodström, R. Bachrach, R. Bauer, and S. Hag-
ström, Phys. Rev. Lett. 27, 1282 (1970); M. den Boer,
T. Einsteln, W. Elam, R. Park, L. Roelof, and
G. Laramore, Phys. Rev. Lett. 44, 496 (1980); K. L.
Bedford and A. B. Kunz, Phys. Rev. B 25, 2119
(1982).
18The experiments (see Ref. 4) show that when the
oxide layer has grown to be thick enough (exposure
around \( 10^9 \) L. of O.) the surface state reappears. Its
desorption yield can be used to convey information
about the amorphous-to-crystalline transition in the
oxide layer, and the associated defects in the oxide-
metal interface.
19J. Stöhr, L. I. Johansson, S. Brennan, M. Hecht,
and J. N. Miller, Phys. Rev. B 22, 4052 (1980); D. Nor-
21A. P. Mills, Jr., in "Proceedings of the Sixth Inter-
national Conference on Positron Annihilation" (North-
Holland, Amsterdam, to be published).