

Observation of the Amorphous-to-Crystalline Surface Transition in Al-Al_xO_y Using Slow Positrons

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The amorphous-to-crystalline surface transition of Al_xO_y on the Al(111) surface is observed between 650 and 800 K with different O₂ exposures by measuring the positronium (Ps) fraction produced by e^+ impinging on the surface. The data are interpreted in terms of vacancy-type defects in the film or at the metal-metal-oxide interface which as trapping sites for e^+ or Ps. As the ordering process proceeds to completion the trapping centers anneal out and the Ps fraction increases, showing an irreversible transition. This technique provides a new experimental method to study interfaces.

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With the advent of efficient monoenergetic positron sources incorporated in ultrahigh-vacuum systems, it is now possible to study positron interactions with well-characterized surfaces. In a recent series of papers¹⁻⁵ the behavior of positrons at a number of metal surfaces has been reported. In some metals an implanted positron can (i) be reemitted into the vacuum,² (ii) escape with an electron and form positronium (Ps),^{1,3} or (iii) annihilate in the perfect lattice, in a lattice vacancy, or in the surface state.^{4,5} The positron can be thermally activated from this surface state and the depth of the potential well can be deduced.⁴⁻⁶ In all clean metals studied the formation of Ps has been found to be the dominant mechanism for the escape of positrons from a metal-vacuum interface.

In the present study we have exposed an Al(111) single-crystal surface to molecular oxygen (O₂). The fraction of Ps produced at room temperature increased initially with increasing O₂ exposures saturating at less than 500 L O₂ (1 langmuir = 1L = 10⁻⁶ Torr sec) and subsequently decreased at larger oxygen exposures. After separate total exposures of 500 L and 10⁶ L O₂, the surface was examined with low-energy positrons as a function of sample temperature, at various incident positron energies, E . When the temperature at which the transition from amorphous to ordered Al_xO_y occurs at the surface the Ps fraction increases and is identified as the removal of trapping centers (vacancy-type defects) for positrons or Ps.

The experimental details of the apparatus and the method of measurement have been described elsewhere.³ In this experiment the existence of Ps (bound electron-positron state) is detected by observing changes in the energy spectrum produced by the *three-photon emission* that occurs upon the decay of orthopositronium (³S₁).⁷ The

incident positron energy was varied by biasing the target at different voltages. The sample was cleaned by repeated cycles of Ar-ion bombardment and annealing (>400 C). Surface characterization was performed by low-energy electron diffraction (LEED) and Auger-electron spectroscopy (AES). Before the sample was exposed to O₂, no detectable impurities were observed by AES. The samples were maintained in a vacuum of $\sim 1 \times 10^{-10}$ Torr during the experimental run (<8 h) except for those periods of O₂ exposure. After each run AES spectra were taken again and no detectable impurities, other than oxygen, were observed. Thus the behavior of the Ps fraction cannot be attributed to impurities diffusing to the surface at elevated sample temperatures or to the desorption of oxygen at the higher sample temperatures.

Figure 1 shows the results obtained on a clean Al(111) crystal. The initial increase in the Ps fraction with temperature has been ascribed to the thermal desorption of positrons bound in a potential well at the sample surface.^{4,5} In this case we find an activation energy for detrapping on the Al(111) of 0.33 ± 0.02 eV in good agreement with Mills.⁴ At higher sample temperatures and incident positron energies the effect of positron trapping at monovacancies is reflected in the decrease in the Ps fraction. These trapping sites shorten the effective diffusion length of the positrons, thereby reducing the number of positrons that can diffuse back to the surface and form Ps. In the region near the surface we deduce a vacancy-formation enthalpy⁵ for Al of approximately $E_{1V}^f = 0.62 \pm 0.05$ eV in good agreement with the widely adopted bulk values.⁸

Data from previous experiments show that approximately a monolayer of chemisorbed oxygen forms on Al(111) at 100 L; therefore 500 L

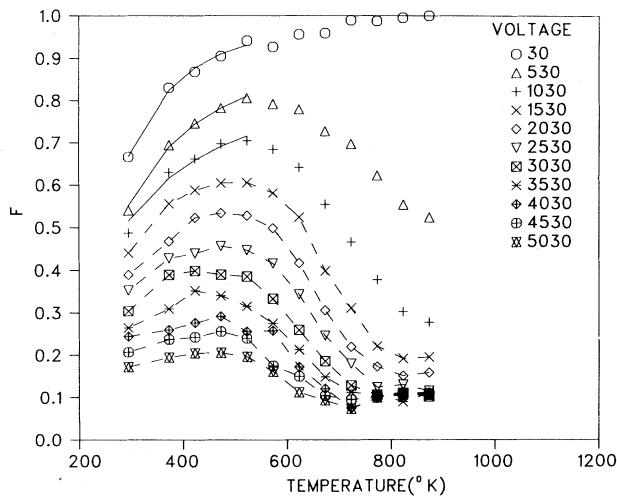


FIG. 1. The fraction of incident positrons converted to *o*-Ps as a function of sample temperature and different incident positron energies for Al(111) surface. The solid lines are least-square fits to the data providing an activation energy for thermal desorption of the positron from the surface state (Refs. 4 and 5). Sharp LEED patterns were observed on the Al(111) surface.

should ensure at least one monolayer of oxygen on the surface.⁹⁻¹¹ Bianconi *et al.*¹² found that the shape of the valence band and the core-level photoemission spectra change after the amorphous-to-crystalline phase transition (~700 K).

Figures 2 and 3 show the Ps fraction versus temperature on the Al(111) surface at various incident positron energies after separate exposures to 500 and 10⁶ L of O₂, respectively. A noteworthy feature is that for low oxygen exposures (500 L) the chemisorbed oxygen removes signs of the surface trap as indicated by an increased Ps fraction at the lower temperatures. This Ps fraction subsequently decreases at higher oxygen exposures (> 500 L) indicating the formation of trapping centers associated with the amorphous overlayer. This behavior shows that the thermally activated detrapping of positrons or the formation of Ps is associated with the surface and not the bulk properties of the Al and that the Ps fraction is extremely sensitive to impurities on the surface.

The sensitivity of the positrons to the overlayer and its associated interface is increased as the incident positron energy is reduced. Anomalous behavior relative to a clean surface is detected after exposure to oxygen (500 L) between 650 and 800 K at the lower positron energies. The

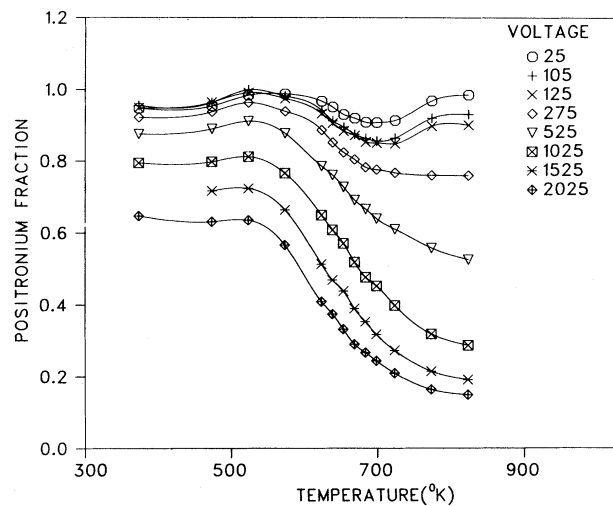


FIG. 2. The fraction of various energy positrons converted to Ps on Al(111) as a function of sample temperature after exposure to 500 L O₂. The sample remained at each temperature for approximately 15 min. More runs were taken at other voltages but are not shown in the figure. After the high-temperature run the Ps fraction was measured with decreasing temperature and no minimum appeared in the region between 600 and 800 K.

low energy ensures us that the positron is interacting with the first few atomic layers. The decrease in the Ps fraction at approximately 600 K for the 500-L case is tentatively ascribed to the

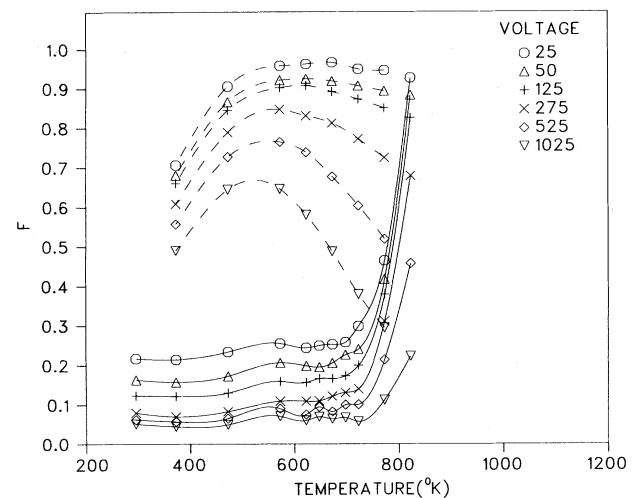


FIG. 3. The fraction of Ps vs sample temperature at various incident energies on the Al(111) surface after exposure to 10⁶ L of ultrahigh-purity O₂. The solid line connects the data points that were taken with increasing temperature whereas the dashed line shows those data that were recorded with decreasing temperature.

formation of the amorphous Al_xO_y containing trapping centers. This decrease can be explained by the generation of trapping centers for positrons or Ps in the initial stages of the formation of the amorphous overlayer. Since Ps, like positrons, may also become localized in the regions of lower than average electron density¹³ (vacancy-type defects), it is not clear which is becoming trapped at these defects. After the observed decrease in the Ps fraction an increase was measured which is associated with the reorientation process to ordered-like $\gamma\text{-Al}_2\text{O}_3$. This increase in the Ps fraction is explained by the removal of these defects thus permitting the Ps or positron to escape more readily into the vacuum, the latter forming Ps while leaving the surface. This behavior is suggested to be directly associated with the phase transition. After the Al(111) sample, exposed to 500 L O_2 , reached the highest temperature the measurements were continued at decreasing temperatures and no minimum was found in the Ps fraction, indicating an *irreversible transition*. Reemission of slow positrons was observed after the sample was cooled to 300 K,¹⁴ showing that the defects were removed thus allowing positrons to diffuse through and escape the overlayer without forming Ps. This minimum in the Ps fraction was also found on an Al(100) sample exposed to 500 L oxygen.¹²

In Fig. 3 the trapping of positrons or Ps associated with the amorphous Al_xO_y can easily be seen by the large decrease in the fraction of Ps atoms decaying by three photons after exposure to 10^6 L O_2 at 300 K. This exposure corresponds to an oxide layer approximately 5 Å thick.¹² It is known that for a 30-Å-thick oxide layer on Al a phase transition occurs from amorphous to crystalline $\gamma\text{-Al}_2\text{O}_3$ at 623 K.¹² These measurements start at 300 K and increase in temperature as shown by the solid line. At the lower incident voltages (<125 eV) and temperatures greater than 700 K one can observe the large increase in the Ps fraction or concomitantly the decrease in the density of trapping centers in the overlayer. Data from recent photoemission experiments¹⁰ show that with 100 L of O_2 a structure similar to the crystalline Al_2O_3 phase appears after the sample temperature has been raised to approximately 700 K. Bianconi *et al.*¹² found that the density of interface states decreases strongly at the metal-crystalline-oxide interface at the same temperature where the increase in the Ps fraction was found. This amorphous-to-crystalline transition was confirmed in this study by LEED after the

sample had been cooled which is in agreement with Martinsson and Flodström.¹⁵

At the higher positron energies and temperatures (≥ 600 K) one can observe those positrons which trap in the thermally generated monovacancies in the underlying Al. From these data one might suggest that this amorphous-to-crystalline transition involves vacancies in thermal equilibrium with the Al sample. Thermal desorption of the positron from the surface state was observed as the sample was cooled at a slightly different temperature than the clean Al. This behavior is presently thought to be associated with the Al_2O_3 surface state and the similarity of this behavior to clean Al(111) is ascribed to an Al-rich outermost layer.

It should be noted from standard positron-lifetime measurements that only a few percent of *o*-Ps decaying by three photons is detected in bulk Al_2O_3 .¹⁶ In this study it is not clear whether the Ps signal is formed in or while escaping the overlayer. If formed in the overlayer, Ps could also be trapped in the amorphous region exhibiting a behavior similar to positron trapping where by a pickoff process occurs and the Ps decays by two photons. After the defects had been thermally removed the *o*-Ps could then form and diffuse through the overlayer into the vacuum in a short time compared to the pickoff rate then decay by three photons. This latter possibility is, however, not completely correct as some free-positron reemission was observed after the Al(111) + 500 L O_2 crystal was cooled from the highest temperatures. All of the present data indicate that irreversible changes occur with temperature in the first few atomic layers, consistent with an amorphous-to-crystalline Al_xO_y phase transition as can be seen in Figs. 2 and 3. It would be useful to correlate the changes in the Ps fraction with electron tunneling measurements in the temperature region between 600 and 800 K. It is noteworthy that the expected kinetics of a temperature-activated recrystallization process are consistent with the Ps-fraction data.¹⁴

These results show for the first time that slow positrons are sensitive to chemisorbed layers and to traps associated with interfaces. Trapping is observed after exposure to 10^6 L O_2 and is reduced only when the transition to ordered Al_xO_y occurs at the higher temperatures. The exact nature of these trapping sites, i.e., whether or not they are positron or Ps traps, will have to await further experiments. Positrons will provide complementary information to other types

of surface probes, especially when defects are associated with the surface region. An interesting possibility is in the study of two-dimensional melting where defects are predicted to play an important role.

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and P are the count rate in the total and photopeak as determined by a Ge(Li) γ -ray detector. This expression removes any dependence on the positron current, i.e., positron reflectivity. The statistical precision is on the order of ± 0.01 , although uncertainties do exist in the calibration which produces errors on the order of ± 0.10 in f .

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Quantum Diffusion of Positive Muons in Iron

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Muon spin precession in iron has been observed from 300 K down to 3 K. The relaxation rate λ shows a pronounced temperature dependence with minima at 15 and 90 K. A fit with an Arrhenius function yields $E_a = 0.3$ meV below 10 K, 14 meV between 35 and 90 K, and 86 meV between 150 and 300 K. The data indicate that coherent tunneling becomes important below 35 K. The temperature region between 35 and 90 K is dominated by incoherent tunneling while above 150 K the over-barrier hopping process sets in.

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In many respects, the positive muon can be considered as a light isotope of hydrogen; in particular, its diffusion behavior should follow that of hydrogen, the main difference arising from a much smaller mass ($m_\mu = \frac{1}{9}m_p$). This difference is rather unimportant at high temperatures where only moderate isotope dependences are expected but becomes crucial at low temperatures when

tunneling plays the dominant role in the diffusion process. In the present Letter, detailed experimental data are presented which provide evidence for coherent as well as incoherent tunneling at low temperatures. The transition between the two mechanisms is around 35 K.

Muon diffusion can be measured by the motional-narrowing effect in a muon-spin-rotation (MSR)