Image States and Local Work Function for Ag/Pd(111)

R. Fischer, S. Schuppler, N. Fischer, Th. Fauster, and W. Steinmann

Sektion Physik, Universität München, Schellingstrasse 4, W-8000 München 40, Germany

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Two-photon photoemission spectroscopy was employed for an investigation of the image states on Pd(111) with various coverages of Ag. Image states from areas with different thicknesses of the Ag layer can be observed simultaneously. This proves the applicability of the concept of a local work function. The decay length of the wave function of the image state on Ag(111) into the metal was determined experimentally to be 7.6 ± 1.2 Å, and the probability to find the electron in the metal is estimated as 10%.

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The most fundamental property of the surface of a metal is the work function, which is generally defined as the minimum energy needed (at $T = 0$ K) to remove an electron from the metal and to bring it far away from the surface. Despite this simple definition work functions are difficult to calculate theoretically and to determine experimentally [1]. One of the experimental problems lies in the nature of real surfaces, which are not infinitely extended and homogeneous, but contain defects. These can be inherent or introduced deliberately by putting adsorbate atoms on the surface. Most methods to measure the work function determine a value averaged over a macroscopic area of the surface, which may contain terraces of the ideal surface and patches covered by defects or adsorbate atoms. It is, therefore, plausible to ascribe a local work function to each of the homogeneous areas of the surface. This local work function can be measured through the photoemission of adsorbed Xe atoms, which is able to resolve the work function locally up to the size of a Xe atom [2].

In this Letter we investigate the question of what work function and potential an electron feels if it is trapped in front of a metal surface. This situation can occur if the electron cannot penetrate deep into the metal, as is the case in a gap of the projected bulk band structure, and if it cannot leave the surface, because its energy is below the vacuum energy. The electron is attracted to the surface through the image force. The resulting bound states are, therefore, called image states. The important feature in our context is that these states form a series converging towards the vacuum energy [3], which differs from the Fermi energy by the work function. The energy of the image states yields, therefore, information about the surface potential and the work function. For an inhomogeneous surface this raises the following question: Does an electron in an image state feel the macroscopic or a local work function? This addresses also the problem of the lateral extent of the wave function of the image state.

We studied the image states on a Pd(111) surface covered with various amounts of Ag. This system exhibits an epitaxial layer-by-layer growth [4], shows a large work function change, and image states have been observed for Pd(111) [5] as well as for Ag(111) [6]. Besides the question raised above, it is interesting to see at

which thickness of the Ag film the image-state series of the Ag(111) surface is reached. This gives direct information about the penetration of the wave function of the image state into the metal.

High-resolution spectroscopy of the image states has been done with two-photon photoemission (2PPE) [7,8]. The basic mechanism is illustrated on the left-hand side of Fig. 1 for the case of the clean Pd(111) surface in normal emission. A photon of energy $2h\nu$ excites an electron from the continuum of bulk states (shaded areas) below the Fermi energy E_F into the first image state ($n = 1$). A second photon of energy $h\nu$ can lift this electron above the vacuum energy E_{vac}, so it can leave the surface. An energy analysis of the electrons emitted normal to the surface gives the spectrum shown at the top of Fig. 1. Note that the low-energy cutoff of the spectrum appears
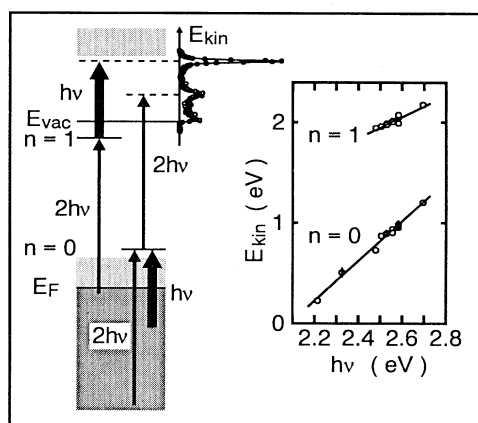

FIG. 1. Excitation scheme of 2PPE in normal emission: The $n = 1$ image state is populated from the continuum of bulk states below E_F (dark shaded areas) after absorption of a photon of energy $2h\nu$, and is ionized with energy $h\nu$. A photon of energy $h\nu$ or $2h\nu$ can excite an electron into the $n = 0$ surface state which is ionized with energy $2h\nu$. A spectrum for $h\nu = 2.53$ eV is shown at the top. Inset: The photon-energy dependence of the kinetic energy for the $n = 0$ and the $n = 1$ states. The slopes of the linear fits of 1.98 ± 0.08 for the $n = 0$ state and of 1.06 ± 0.05 for the $n = 1$ state verify that the second excitation step for these states is performed by $2h\nu$ and $h\nu$ photons, respectively.

at E_{vac} and yields directly the macroscopic work function [8,9].

Experimental details have been published previously [7,8]. The photons come from the ground wave and the frequency-doubled wave of a tunable dye laser which is pumped by an excimer laser. The hemispherical electron-energy analyzer was used with an energy resolution of 45 meV. The sample was cleaned by Ne^+ sputtering and heating followed by repeated oxidation-heating cycles to 900 K to remove residual carbon. The sample preparation was checked with Auger electron spectroscopy (AES), thermal-desorption spectroscopy, and low-energy electron diffraction (LEED). Ag was evaporated from a tungsten basket at a rate of 0.01 monolayer (ML) per second onto the Pd(111) substrate at room temperature and at a pressure of $< 3 \times 10^{-10}$ mbar. The coverage was controlled by the deposition time and was checked by work-function and AES measurements. For the absolute calibration the AES data were compared to the results of Eisenhut et al. [4].

First we are going to discuss the clean Pd(111) surface. On this surface an unoccupied surface state exists, which is denoted $n = 0$ in Fig. 1. Because of its energetic position near E_F the excitation process is different from that for the image states. A photon of energy $2h\nu$ is needed to excite the electron above E_{vac}. As shown on the right-hand side of Fig. 1 the kinetic energy E_{kin} changes twice as much with photon energy $h\nu$ compared to the image state which is excited by a photon of energy $h\nu$. The energy of the $n = 0$ state is 1.26 ± 0.03 eV above E_F. From the low-energy cutoff we obtain the work function Φ as 5.44 ± 0.03 eV. The $n = 1$ image state then has a binding energy of 0.55 ± 0.03 eV relative to E_{vac} and its intrinsic width as determined from a line-shape analysis [9] is 70 ± 20 meV. The width of the $n = 2$ state (not shown in Fig. 1) is significantly smaller, and its binding energy is 0.15 ± 0.03 eV. These values supersede the less precise previous measurements [5,10] and agree moderately with parameter-free first-principles calculations [11].

In Fig. 2 we show 2PPE spectra for Ag coverages between 0 and 2.0 ML on Pd(111). The energy scale is relative to E_F. We observe that the $n = 1$ state for the clean surface at 4.89 eV disappears at 1.0 ML and that a new state with an energy of 4.13 eV appears already at 0.1 ML. This peak is the dominant feature for coverages between 0.5 and 1.5 ML and has disappeared at 2.0 ML. At this point only a peak at 3.95 eV is visible which can be observed in Fig. 2 from 1.35 ML on. These new states lie independently of coverage always at a fixed energy relative to E_F and are best developed at the completion of a layer. We assign these peaks to the image states for 1 and 2 ML of Ag on Pd(111). For intermediate coverages two $n = 1$ states can be observed from areas with different layer thickness. The fact that for complete layers only one state is observed confirms the layer-by-layer growth and our calibration of the coverage. The assignment of
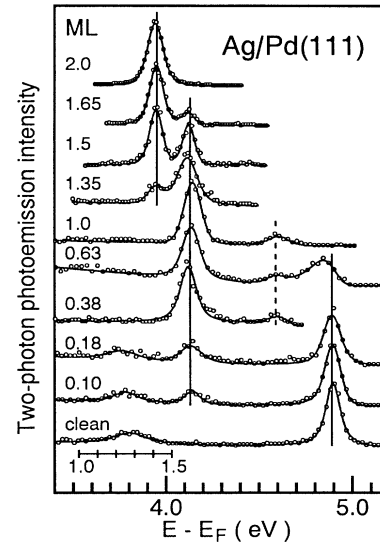

FIG. 2. Series of 2PPE spectra showing the evolution of the image states as a function of Ag coverage on Pd(111). The photon energies vary between 2.18 and 2.53 eV. The inserted scale is valid only for the $n = 0$ state seen for the lowest three coverages.

the states to image states is confirmed by the observation of a series of states. In Fig. 2 the $n = 2$ state for 1 ML Ag can be seen at 4.59 eV which is below the $n = 1$ state for clean Pd(111). The narrow linewidth observed at all coverages is also characteristic for image states [9].

For the discussion of these results we plotted in Fig. 3 the energies of all observed states relative to E_F as a function of coverage. The constant energies of the vari-
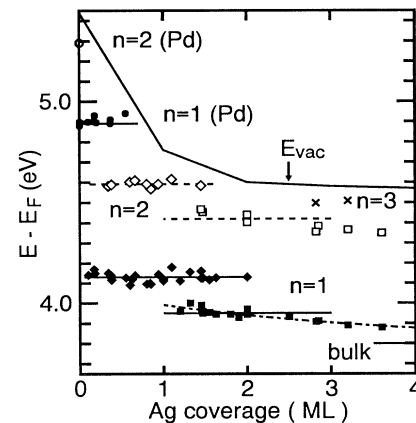

FIG. 3. Energies of the image states as a function of the Ag coverage on Pd(111). Average values are shown by the horizontal lines (solid, $n = 1$; dashed, $n = 2$). The dot-dashed line is the result of a fit to the data for the $n = 1$ state for coverages above 2 ML and converges to the value for bulk Ag. As symbolized by a line the vacuum energy E_{vac} decreases linearly for coverages between the completed layers.

ous states within the respective coverage ranges can be seen clearly. We found the work function to vary linearly between the coverages of the completed monolayers. This macroscopic work function determined from the low-energy cutoff of the spectra averages over the patches with different thicknesses of the Ag film. The image states feel a local work function corresponding to the individual patch at which the electron is trapped. The minimum size of the patches can be estimated from the distance of the maximum of the wave function away from the surface [2]. For the $n=1$ (2) state this gives that the mean radius of the patches must certainly be greater than 4 (10) Å [3]. Smaller patches would result in an additional broadening of the linewidth for the $n=1$ state by ≥ 60 meV [9], which is not observed at any coverage (see Fig. 2). A LEED spot-profile analysis for this system shows that the patches have a diameter of more than 100 Å at all coverages [4].

For completed layers the measured and the local work function should coincide, and we can determine the binding energies of the image states relative to E_{vac} (see Table I). The energy for the $n=1$ state varies from 0.55 eV for Pd(111) to 0.75 eV for a thick Ag film in good agreement with 0.77 eV reported for the clean Ag(111) surface [6]. The concept of the local work function and the correct values of the work function for the completed monolayers can be checked in the following way: It is well known that the binding energies of the image states can be described by $E_b^n = (0.85 \text{ eV})/(n+a)^2$, where a is a quantum defect independent of n [3,7]. From the measured energy difference between the $n=1$ and the $n=2$ state we can determine the quantum defect a. By combining the energy of the $n=1$ state (which is measured relative to E_F)

with $E_b^{n=1}$ from the quantum defect formula we can determine the local work function at any coverage. The values extrapolated in this way agree very well with the work function measured for the completed layers (see Table I).

For coverages above 2 ML the energies of the states for different layer thicknesses cannot be resolved. For intermediate coverages we, therefore, measure an average value of the energies for the nearest completed layers. The energies of the $n=1$ states approach with increasing coverage θ the asymptotic value of 3.80 eV as $\delta\exp(-\theta/\lambda)$. A fit of the data in the coverage range from 1.2 to 18.0 ML yields a prefactor $\delta=0.26 \pm 0.02$ eV and a decay length $\lambda=3.2 \pm 0.5$ ML (see the dot-dashed line in Fig. 3). In first-order perturbation theory we can estimate the energy correction as a function of coverage, if we regard the system of j layers of Ag on Pd as an Ag crystal whose potential V_{Ag} is changed to the Pd potential V_{Pd} after j layers. Above 2 ML the energies of the $n=1$ states are just below the upper edge of the Ag band gap [12], and the wave function for a thick Ag film can be approximated within the two-band model as $\psi(z) =\exp(-z/\lambda)\sin(\pi z/d)$ with the layer separation $d=2.36$ Å and the decay length $\lambda=6.1$ ML [3,12]. Using the potential parameters from Ref. [12] we obtain $\langle\psi|V_{Pd}-V_{Ag}|\psi\rangle=(2.6 \text{ eV})\exp(-2j/\lambda)$ if we normalize the wave function in the Ag crystal to 1. This expression predicts the energy correction to decay on a length scale of $\lambda/2=3.0$ ML, which is in good agreement with the experimental value. From the ratio of the prefactors we conclude that the probability to find the electron inside the crystal is about 10%. This number agrees with theoretical estimates [9], but is relatively uncertain since

TABLE I. Measured work function Φ, energy of the $n=0$ state relative to E_F, and binding energies of the image states for completed layers of Ag on Pd(111). The measured binding energies were used to determine the extrapolated work function within the quantum defect model. All values are in eV and the experimental uncertainties are ± 0.03 eV. Results of a one-dimensional model calculation are also given.

			Ag (ML)			
	Pd(111)	1	2	3	4	12
Φ						
Experimental	5.44	4.76	4.60	4.58	4.57	4.55
Extrapolated	5.46	4.77	4.61	4.56	4.54	4.57
$n=0$						
Experimental	1.26	$\cdots$	$\cdots$	<0	<0	<0
Calculated	1.17	0.99	0.13	-0.02	-0.08	-0.11
$n=1$						
Experimental	0.55	0.63	0.65	0.68	0.71	0.75
Calculated	0.58	0.63	0.67	0.70	0.71	0.75
$n=2$						
Experimental	0.15	0.17	0.18	0.21	0.22	0.18
Calculated	0.18	0.19	0.19	0.20	0.20	0.21
$n=3$						
Experimental	$\cdots$	$\cdots$	$\cdots$	0.08	0.10	0.10
Calculated	0.08	0.09	0.09	0.09	0.09	0.09

it depends on the difference of the potential parameters.

For a quantitative interpretation of the binding energies at full monolayer coverages we performed calculations using a one-dimensional model without adjusting any parameters. The bulk wave functions are represented within the two-band approximation [3] using the band-gap parameters for Ag and Pd as given in the literature [12]. The wave function decaying into the Pd bulk is matched at the Pd/Ag interface to the two linearly independent solutions (decaying and increasing) in the Ag layer. For the wave-function matching at the vacuum interface the WKB phase shift [3] was used to describe the behavior of the wave function of the image state at the interface. The results of these calculations are presented in Table I and agree well with the experimental data. The calculations predict that the $n = 0$ state becomes occupied above 3 ML. Because of emission from the Pd d bands the $n = 0$ state could not be observed in regular photoemission experiments. However, 2PPE spectra exhibit an anomalously high intensity of the $n = 2$ state relative to the $n = 1$ state for coverages above 3 ML, which can be explained by resonant excitation from the $n = 0$ state below E_F into the $n = 2$ state [7,13]. This observation indicates the existence of the $n = 0$ state below E_F and is denoted by an energy " < 0" in Table I.

In conclusion, we have shown that 2PPE of image states can be used to measure the local work function on the homogeneous areas of a surface. This method has been used recently to determine the proper work function of alkali monolayers [13]. A study of the behavior of the image states as a function of the size of the homogeneous patches is currently in progress.

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