

Coupling of image states to quantum-well states for Au on Pd(111)

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With two-photon photoelectron spectroscopy we have investigated the image states on a Pd(111) surface with Au coverages up to 10 ML. The energies of the image states are strongly influenced by the quantum well of the Au layers. The coupling of the image states to the quantum-well states is described by one-dimensional model calculations that reproduce the experimental results quantitatively.

One of the simplest examples for quantum-mechanical effects is the particle-in-a-box model. Physical realizations of this model can be found in layered semiconductor structures¹ or in thin metal films.²⁻⁸ The electron is confined to the layer and stationary states develop in the potential of the quantum well. A different type of localization may occur for electrons in front of a metal surface. The concept of the image charge leads to a force which can be derived from an attractive $1/z$ potential. An infinite series of bound states converging towards the vacuum level E_{vac} forms if the electron cannot penetrate the metal due to a band gap along certain directions.⁹ For the interpretation of photoemission experiments on thin metal films an influence of the image potential outside the surface has been found in calculations of quantum-well states.^{2,5-7} Inverse photoemission work for Fe on Au(100) concentrated on the quantum-well states and did not discuss a possible coupling to image states in the same energy range.⁸ The case of quantum-well states degenerate with image states has not been addressed so far, neither theoretically nor experimentally, and will be the subject of this article.

Quantum-well states are standing waves in the overlayer of thickness d with the wave vector

$$k = (2\pi j + \varphi_l + \varphi_r)/2d, \quad j = 0, 1, 2, \dots \quad (1)$$

The number of extrema of the wave function in the quantum well is $j+1$. The phases φ_l and φ_r describe the phase shifts⁶ at the reflection by the left and right boundaries of the quantum well, respectively. For an infinitely high potential barrier the phase shift is π . The energy of a state with wave vector k is

$$E = \hbar^2 k^2 / 2m^* \quad (2)$$

relative to the bottom of the quantum well with an effective mass m^* describing the motion of the electron in the solid. For an overlayer the bulk band structure can be used with an appropriate choice of the band edge as the origin of the energy and wave-vector scale.^{6,8} In this case k represents the wave vector of the envelope function. Figure 1 shows the energy ranges spanned by the $j=0$ and $j=1$ states for a layer thickness of 6 ML and a variation of the total phase $\varphi_l + \varphi_r$ between 0 and 2π . The upper band edge and the zone boundary are chosen as the origin of the energy and the wave-vector scale,

respectively.

The image states form a hydrogenic series of bound states converging towards E_{vac} with energies⁹

$$E(n) = E_{\text{vac}} - 0.85 \text{ eV} / (n+a)^2, \quad n = 1, 2, \dots \quad (3)$$

The quantum defect a would be zero for an infinitely high barrier and changes from zero to $1/2$ across the gaps (top to bottom), which exist in the band structure of a metal only along certain directions. The quantum defect a is related to the phase shift φ_C upon reflection at the surface⁹

$$a = 1/2 (1 - \varphi_C/\pi). \quad (4)$$

The energy of the lowest ($n=1$) image state can vary only between 0.85 and 0.38 eV [Eq. (3)] in contrast to the energy of the first quantum-well state, which can change with layer thickness d over a wide range [Eqs. (1) and (2)]. This provides a convenient way to reach the situation where an image state and quantum-well state are close in energy.

We have studied the system of thin Au films on Pd(111). There is a large band gap around E_{vac} for

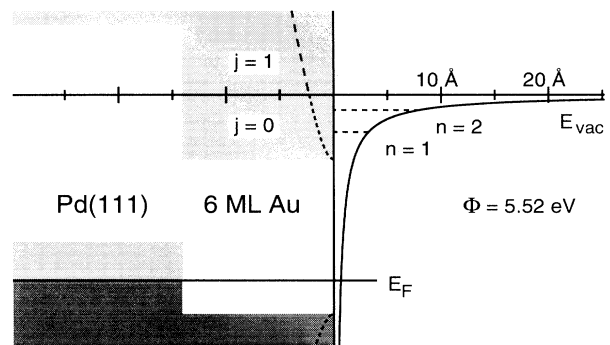


FIG. 1. Schematic image potential and projected bulk bands (shaded areas) for 6 ML of Au on Pd(111). The energy bands of Au(111) are indicated by the dashed lines with the origin at the interface and the zone boundary at the surface of the Au layer. By a variation of the phases φ in Eq. (1) the energy ranges indicated by the short and long dashes are covered by the $j=0$ and $j=1$ quantum-well states, respectively.

Pd, whereas the upper edge of the band gap for Au is ~ 2 eV below E_{vac} (Fig. 1). The work function^{10–12} and the energy of the first image state relative to the Fermi level E_F (Refs. 10 and 13) are very similar for Pd(111) and Au(111). Consequently, only small variations of these quantities with coverage should be expected. Due to the small lattice mismatch ($\approx 5\%$) between the two fcc materials, epitaxial growth is expected. At room temperature a layer-by-layer growth has been reported¹⁴ with pseudomorphic Au layers for coverages up to 3 ML.¹⁵ The Pd(111) crystal was prepared by standard techniques.^{10,15} Gold was evaporated from a resistively heated tungsten basket. Deposition and measurements were performed with the substrate at room temperature. Coverages were calibrated by Auger electron spectroscopy relative to the work of Eisenhut¹⁵ using the same crystal.

The experimental technique with the best energy resolution and surface sensitivity for the study of image states is two-photon photoelectron spectroscopy.¹⁶ A photon is used to excite an electron out of an occupied state into the image state. A second photon excites the electron above E_{vac} . It can then leave the surface and its energy and direction can be measured by conventional techniques of electron spectroscopy. In this work an energy resolution of 45 meV was used and only electrons traveling along the direction parallel to the surface normal were detected. The low-energy cutoff of the spectra corresponds to electrons leaving the sample with negligible kinetic energy and can be used to determine the work function $\Phi = E_{\text{vac}} - E_F$ of the sample.¹⁶ Because the second excitation step has to occur within the lifetime of the electron in the image state, high photon intensities are necessary. In this work the frequency-doubled and the fundamental wave of a dye-laser system have been used for the first and second excitation step, respectively.

A series of spectra for Pd(111) with Au coverages ranging from 0 to 10 ML is shown in Fig. 2. The data were taken with a photon energy of 2.58 eV (2.53 eV for 5.7 ML) in the fundamental wave and are plotted relative to E_F . By variation of the photon energy it was checked that the positions of the peaks shown in Fig. 2 correspond to the energies of unoccupied states.¹⁶ The work function is given to the right of each spectrum and shows little variation, as expected. The increase by ~ 0.14 eV for coverages $\lesssim 4.5$ ML might be correlated with the lateral compression of the pseudomorphic Au layers on Pd(111). For a rough surface a lowering of the work function¹² and a quenching of the image states^{16,17} would be expected. The observations indicate a smooth surface in agreement with a layer-by-layer growth mode.¹⁴

The image states show much more dramatic changes as a function of coverage, in contrast to the work function. The sharp peak at 4.89 eV for clean Pd(111) shows no shift in energy for small coverages. The peak becomes narrower with an intrinsic linewidth of 40 ± 20 meV at 1 ML compared to 70 ± 20 meV for the clean surface.¹⁰ The explanation is the quenching of the unoccupied surface state,¹⁰ (not shown here) which eliminates an important decay channel for the image state.¹⁷ For coverages above 1 ML the peak broadens considerably and shifts to lower

energy. At 5.7 ML, intensity in the energy range from 4.3 to 5.1 eV (Ref. 18) is seen with a maximum corresponding to a binding energy of ~ 1 eV relative to E_{vac} . This value is outside the regime covered by positive quantum defects a in Eq. (3). At 6.2 ML, only one peak at 4.93 eV remains, which shifts down in energy until a value of 4.75 eV characteristic for the clean Au(111) surface¹³ is reached around 10 ML. The large width of the peak also agrees with measurements for Au(111) and is explained by its energetic position outside the band gap making it an image resonance¹³ with a shorter lifetime¹⁶ than an image state.

The unusual behavior of the states seen in Fig. 2 around 6 ML could be correlated with structural changes. In this coverage regime the Au films change their lattice constant from the Pd to the Au value.¹⁵ Low-energy electron diffraction patterns indicate no reconstruction, but show an increase of the background. Heating of the 6.2 ML film to 425 K did not change the two-photon photoelectron spectrum and increased the work function slightly by 0.03 eV. This means that a (meta)stable configuration of the films is already reached at room temperature. An alloying of the films is observed at annealing temperatures above 500 K.^{19,20}

The concept of the local work function¹⁰ implies the simultaneous observation of image states from terraces of different heights. This holds as long as the terraces are large enough.²¹ An explanation of the wide spectrum for 5.7 ML within this model would require large variations

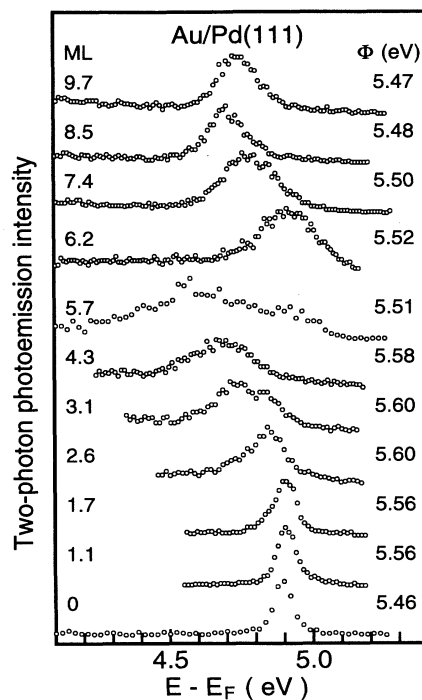


FIG. 2. A series of two-photon photoelectron spectra with increasing Au coverage on Pd(111). The energies of the unoccupied states are given relative to the Fermi level. The coverage and work function is given to the left and the right of each spectrum, respectively.

of the local work function and image-state energy with terrace height. However, for Au on Pd(111) no drastic change in the work function is observed and the image-state energy (relative to E_F) varies only from 4.89 eV [Pd(111) (Ref. 10)] to 4.75 eV [Au(111) (Ref. 13)]; see also Fig. 2]. This would lead to an image state with a wave function spread over the whole surface because the small potential barrier is not sufficient to localize the electron on a specific island.²¹ An imperfect layer-by-layer growth and the defects related to the compensation of the lattice mismatch would explain the large width of the peaks. The larger penetration into the gold film in the absence of a band gap would also result in a shorter lifetime of the states and, consequently, a larger linewidth.¹⁷ These interpretations cannot explain, however, the large binding energies.

The explanation for the observed behavior with coverage is related to the larger penetration. The wave function of the electron can be reflected at the interface between the Au film and the Pd substrate. The resulting standing waves correspond to quantum-well states. For 6 ML the energy of the $j = 0$ state is expected to fall in the energy range of the image states, as indicated by the short-dashed energy band shown for the Au layer in Fig. 1. The energy depends on the phase shifts in Eq. (1). A strong influence on the image state by the wave function in the Au layer is expected and observed. This is illustrated in Fig. 3 by the wave functions calculated within a one-dimensional scattering model using only the band-structure parameters for Pd(111) and Au(111) and no additional parameters.²² The states are numbered by ν according to their energy and do not necessarily correspond to image states numbered by n in Eq. (3). An example is the wave function of the $\nu = 2$ state for 6 ML Au on Pd(111), which is in the vacuum region very similar to the $\nu = n = 1$ wave function on the clean Pd(111) surface. Both states have also very similar binding energies relative to the vacuum level. The lowest $\nu = 1$ state for the Au-covered surface has a considerably larger binding energy, in agreement with the experimental data. Its wave function extends much less into the vacuum, so it has more the character of a quantum-well state which is influenced by the image potential. The image potential plays an important role on the energy and the wave function of this state, which has a probability of 34% to find the electron outside the crystal (see Fig. 3). For the $\nu = 2$ state this probability is 58%.

The detailed behavior of the calculated states is shown in Fig. 4. With increasing coverage the $\nu = 1$ state is pulled down in energy, in agreement with the experimental data. Around 6 ML the $\nu = 2$ state takes over the image-state character and the $\nu = 1$ state becomes more a quantum-well state. In the calculations this can be checked because the latter are less influenced by the work function, in contrast to the image states. The $\nu = 1$ quantum-well states lose intensity for coverages above ~ 6 ML. This is probably due to a shorter lifetime of these states, which have most of their wave function in the metal. In the calculations this can be modeled by the introduction of an imaginary part of the potential. A value of 0.4 eV makes the $\nu = 1$ state disappear for

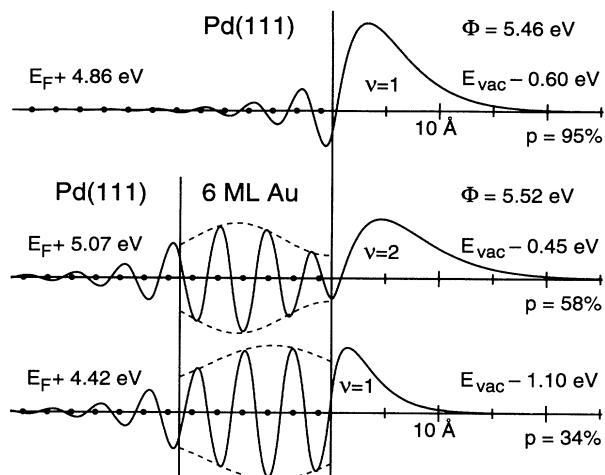


FIG. 3. Calculated wave functions for 6 ML of Au on Pd(111) and clean Pd(111). The dashed lines represent the envelope functions (Refs. 6 and 8) for the quantum-well states in the Au layer. The position of the atoms is indicated by the filled circles. The energies of the states and the probability p to find the electron outside the surface are given.

higher coverages. This value is within the range known from other calculations²³ and measured linewidths for bulk states.¹⁶ The imaginary part has only little influence (< 0.1 eV) on the calculated energies.

The presented example shows that the distinction between image states and quantum-well states becomes difficult when they are close in energy. A simple criterion might be the probability to find the electron outside the layer, but this quantity varies with layer thickness. It also depends on the energetic position relative to the band gap of the substrate and is particularly high for Pd(111) with E_{vac} near the center of the band gap. A binding energy of more than 0.85 eV relative to E_{vac} , implying a negative quantum defect a in Eq. (3), gives an unambiguous test to exclude image states. The changes in the energies are not due to a hybridization between electronic states

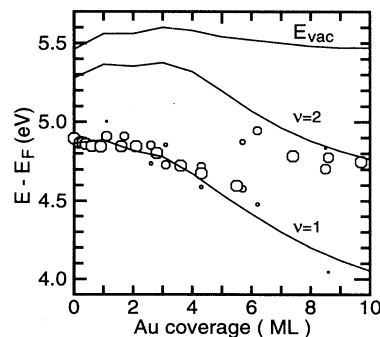


FIG. 4. Vacuum energy and experimental and calculated energies of the unoccupied states as a function of Au coverage on Pd(111). All energies are relative to the Fermi level. The size of the symbols indicates the relative peak intensities for spectra where two peaks are observed.

of the surface and the quantum well. The energies of both states are not fixed in energy and shifted by the interaction, but can vary over a considerable energy range. The relevant property is the boundary condition at the surface, which can be conveniently formulated within the concept of the phase shift.^{9,6} The metal overlayer introduces a phase shift which changes with coverage (and energy). This has a direct effect on the quantum defect [Eq. (4)] and the binding energy [Eq. (3)]. These equations can still be applied because the image potential outside the surface is independent of the substrate or overlayer.

In summary, we have shown that the coupling between quantum-well states and image states leads to another type of states. These have been identified experimentally through their anomalous binding energies. Theoretical

model calculations confirm the data and show that under the right conditions the wave function has maxima of similar magnitude outside the surface and in the overlayer. The electron is then found with equal probability in both regions. The surprising fact is that the image state, as an extreme case of a surface state, actually carries information on the properties of the bulk substrate or an overlayer.

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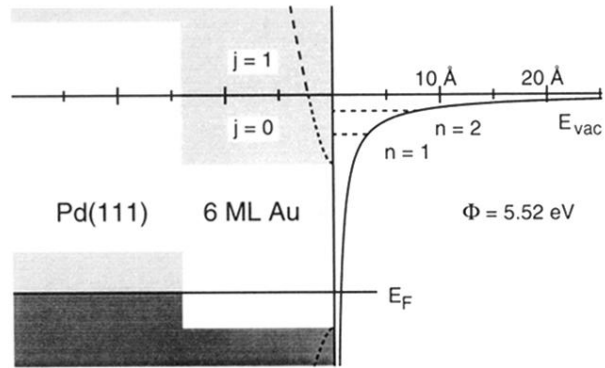


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