GROWTH AND MORPHOLOGY OF ULTRATHIN METAL FILMS STUDIED
BY THE HIGH-RESOLUTION SPECTROSCOPY OF IMAGE STATES
THROUGH TWO-PHOTON PHOTOEMISSION

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ABSTRACT

Electrons can be loosely bound to metal surfaces by the attractive image potential. The image states constitute a very sensitive probe of the surface potential and are studied with high resolution by two-photon photoelectron spectroscopy. During the growth of ultrathin metal films, image states from different layers can be distinguished by their local work function. This allows to identify layer-by-layer growth and other growth modes. The changes of the morphology of the films during annealing and the formation of surface alloys can be monitored. Localization of image-state electrons on small islands results in energy shifts from which the island-size distributions can be derived. Localization perpendicular to the surface is observed by the coupling of image states to quantum well states in thin metal films. Because image states are not involved in the metallic or chemical bonding, they provide the perfect test electrons for a sensitive probe of surface properties.

1. Image States

The screening of an electron placed at distance \( z \) in front of a metal surface leads to a field outside the surface which is identical to the one produced by an opposite charge placed at a distance \( 2z \) away (Fig. 1). The attractive image force between the electron and its image charge can be derived from a Coulomb-like potential approaching the vacuum energy \( E_{\text{vac}} \) for large distances:

\[
V(z) = E_{\text{vac}} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{4z}.
\]

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Figure 1: Top: The electric field of an electron in front of a metal surface can be described by the concept of an image charge. Bottom: The corresponding attractive image potential leads to a series of bound states if the electron cannot penetrate into the metal along certain directions due to a band gap. For the lowest two states the square of the wave function is shown.

In metals, band gaps may exist along certain directions which forbid the penetration of the electron into the metal and bound states may form. The quantum-mechanical solution of this one-dimensional Coulomb problem leads to an infinite series of bound states (numbered by \( n \)) converging towards \( E_{\text{vac}} \) with energies

\[
E(n) = E_{\text{vac}} - 0.85 \text{ eV}/n^2, \quad n = 1, 2, \ldots
\]  

(2)

The factor of 4 in the denominator of Eq. 1 leads to a corresponding expansion of the length scale and a reduction of the binding energies of the image states by a factor of 16 compared to the hydrogen atom. The maximum of the wave function of the lowest state is typically one interatomic distance away from the surface (see Fig. 1).
2. Two-photon photoemission

The best experimental technique for the study of image states is two-photon photoelectron spectroscopy (2PPE). Figure 2 illustrates the bichromatic mode of 2PPE. A photon of energy $2h\nu$ produced by a laser system is used to excite an electron from the occupied states below the Fermi level $E_F$ into the image state. A second photon of energy $h\nu$ may lead to the photoemission of the electron. An electron spectrometer detects the electron with high energy resolution (< 25 meV). In this work only spectra for electrons leaving the sample within 0.6° along the surface normal are shown. The binding energy of the image states relative to $E_{\text{vac}}$ is readily obtained from the low-energy cutoff of the spectrum at the top of Fig. 2 which corresponds to electrons leaving the sample with negligible kinetic energy. This yields also accurate values of the work function $\Phi = E_{\text{vac}} - E_F$ of the sample.

![Figure 2: Schematic energy diagram for the excitation steps in two-photon photoemission. Spectra record the emitted electrons as a function of their kinetic energy.](image)

3. Clean surfaces

Figure 3 presents 2PPE spectra for the (111) surfaces of Au, Ag, and Pd on an energy scale relative to $E_{\text{vac}}$. All spectra show very little background and narrow peaks. The second peak at higher energy seen for Ag and Pd is due to the $n = 2$ image state. The binding energies of the $n = 1$ peaks deviate significantly from the value of 0.85 eV predicted by Eq. 2 with a deviation of 0.30 eV for Pd(111). The energies of the $n = 2$ are also observed with smaller binding energies than expected.
The introduction of a quantum defect $a$ into Eq. 2

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

leads to a very good description of the image-state series for all clean metal surfaces.\textsuperscript{2}

The deviation of the binding energies can be related empirically to the energetic position of the image states within the band gap as shown in Fig. 4. The results of calculations of a one-dimensional scattering model\textsuperscript{5} are shown as lines. From these curves the quantum defect $a$ of Eq. 3 can be determined. There is generally very good agreement between the experimental data and the results of the calculations. An exception occurs for the ferromagnetic surfaces which have higher binding energies than expected. An explanation might be larger self-energy corrections for these materials.\textsuperscript{6}

The relation between binding energy and energetic position within the band gap can be understood by considering the part of the wave function inside the surface. In Fig. 1 the penetration of the wave function into the bulk has been neglected. For energies within the band gap the correct wave function decays exponentially into the bulk and has to be matched at the surface to the solution in the vacuum region. This is illustrated in Fig. 5 which shows that the $s$-like bulk solution for energies at the
Figure 4: Measured (symbols) and calculated (lines) binding energies of image states as a function of their energetic position relative to the band gap.

Figure 5: Wave functions of $n = 1$ image states as a function of their energetic position relative to the band gap. The matching conditions at the surface push the maximum away from the surface leading to a decrease in binding energy going from the top to the bottom of the band gap.
top of the band gap has a node at the surface so it can be matched to the solution similar to the hydrogen atom. For energetic positions lower in the band gap the wave function has a finite amplitude. The boundary condition at the surface pushes the maximum of the wave function further away from the surface plane into a region of weaker image potential resulting in a reduced binding energy. The quantum defect changes from zero to 1/2 across the gap (top to bottom).\textsuperscript{7} For the $n = 1$ image state, only binding energies between 0.38 and 0.85 eV are expected within this model and observed for clean metal surfaces (see Fig. 4).

4. Metal overlayers

For metal overlayers on a metal substrate the concept of the image charge is still valid and image states can exist. Their dependence on thickness and growth mode of the film will be the subject of this section.

![Figure 6: Series of two-photon photoelectron spectra with increasing Au coverage on Pd(111). The energies of the unoccupied states are plotted relative to the Fermi level. The coverage and work function are given to the left and right of each spectrum, respectively.](image-url)
4.1. Au / Pd(111)

A particular simple system seems to be Au on Pd(111). The work function as well as the energy of the first image state relative to $E_F$ differ between Pd(111) and Au(111) by less than 0.15 eV. The small lattice mismatch ($\approx 5\%$) between the two fcc materials leads to an epitaxial layer-by-layer growth at room temperature.

A series of spectra for Pd(111) with Au coverages ranging from 0 to 10 ML is plotted relative to $E_F$ in Fig. 6. The work function is given to the right of each spectrum and shows little variation. The slight increase at low coverages indicates a smooth surface. The image states show considerable changes as a function of coverage. The sharp peak at 4.89 eV for clean Pd(111) does not just shift down with coverage by 0.14 eV to reach the energy of 4.75 eV observed for 10 ML of Au and for clean Au(111) surfaces. 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 is observed with a maximum at $\sim 1$ eV below $E_{\text{vac}}$. This value is incompatible with positive quantum defects $a$ in Eq. 3. At 6.2 ML only one peak at 4.93 eV is seen, which shifts down in energy until the value of the clean Au(111) surface is reached around 10 ML.

Figure 7: Schematic potential, bands (shaded areas), and wave functions for 6 ML of Au on Pd(111) and the clean Pd(111) surface. The filled circles mark the positions of atoms.
Figure 8: Measured vacuum energy, experimental and calculated energies of the unoccupied states as a function of Au coverage on Pd(111). The size of the symbols indicates the relative peak intensities for spectra where two peaks are observed.

The observed behavior with coverage is explained by the absence of a band gap in the Au band structure in the energy range of the image states (see Fig. 7). The electron is reflected by the Pd substrate and the surface barrier leading to standing waves in the quantum well of the overlayer. The wave functions calculated within a one-dimensional scattering model are shown in Fig. 7. The stationary states are numbered according to their increasing energy. The wave function of the $n = 2$ state for 6 ML Au on Pd(111) resembles in the vacuum region the $n = 1$ wave function on the clean Pd(111) surface. Both states have also very similar binding energies relative to the vacuum level. The $n = 1$ state for the Au-covered surface has a considerably larger binding energy than 0.85 eV in agreement with the experimental data. Its wave function extends much less into the vacuum, so it is more a quantum well state influenced by the image potential.

The detailed behavior of the calculated states is shown in Fig. 8. With increasing coverage the lowest state is pulled down in energy and becomes a quantum well state at higher coverages. Its energy is then less influenced by the work function as can be checked in the calculations. The second state shifts downward and acquires the $n = 1$ image-state character above 6 ML. There is generally good agreement with the experimental data. The size of the symbols indicates at each coverage the relative intensity of the two peaks fitted to the spectra. The quantum well states are seen only with low intensity for coverages above ~ 6 ML which is probably due to a shorter lifetime of these states. For these states the probability to find the electron in the metal is larger than outside the surface.
4.2. Ag / Pd(111)

Between Ag(111) and Pd(111) a large work-function difference and, consequently, a large difference in the energies of the image states relative to $E_F$ exists. In this case the overlayer has a band gap in the energy range of the image states. Spectra for Ag coverages between 0 and 2.0 ML on Pd(111) are plotted in Fig. 9 relative to $E_F$. A new state with an energy of 4.13 eV appears already at 0.1 ML. This peak increases in intensity relative to the $n = 1$ state for the clean surface at 4.89 eV which has disappeared at 1.0 ML. For coverages above 1.0 ML a new peak at 3.95 eV is visible which remains the only peak observed at 2.0 ML. These new states lie always at a fixed energy relative to $E_F$ independent of coverage. They are the only states observed at full monolayer coverages and are the image states for 1 and 2 layers of Ag on Pd(111). In Fig. 9 the $n = 2$ state for 1 layer of Ag can be seen at 4.59 eV which confirms the assignment of the peaks to image states. The narrow linewidth

![Figure 9: Series of two-photon photoemission spectra showing the evolution of the image states as a function of Ag coverage on Pd(111). The energy scale is relative to $E_F$.](image)

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Figure 10: 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 shows the exponential approach of the data for the \( n = 1 \) state for coverages above 2 ML to the value for bulk Ag. The vacuum energy \( E_{\text{vac}} \) decreases linearly for coverages between the completed layers.

observed at all coverages is also characteristic for image states. The fact that for complete layers only one state is observed confirms the layer-by-layer growth. For intermediate coverages, two \( n = 1 \) states can be observed from areas with different layer thicknesses.

The energies of all observed states relative to \( E_F \) as a function of coverage are plotted in Fig. 10. The energies of the various states stay constant within the respective coverage ranges. The vacuum energy determined from the low-energy cutoff of the spectra is also indicated in Fig. 10 and varies linearly between the coverages of the completed layers. This reflects the work function averaged 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.

For completed layers there is no difference between the macroscopic and the local work function. This can be checked by the convergence behavior of the series of image states which is described by Eq. (3). The values for the (local) \( E_{\text{vac}} \) extrapolated in this way agree very well with the work function measured for the completed layers as indicated by the short horizontal lines crossing the curve \( E_{\text{vac}} \) in Fig. 10.

For higher coverages the image states corresponding to islands of different heights cannot be resolved and an average energy is measures. From the exponential approach of the asymptotic value for Ag(111) the wave function of the image state into the metal can be determined.
4.3. Surface morphology

At room temperature Ag grows layer-by-layer on Pd(111). The growth mode might be modified at other temperatures. The spectrum for deposition of 1.0 ML Ag at 90 K in Fig. 11 shows two series of image states and looks similar to the one for 1.35 ML of Ag on Pd(111) in Fig. 9. The series at lower energy comes from two-layer-thick Ag areas, and the other from one-layer-thick areas. The image states of the patches which are not covered by Ag are not seen in Fig. 11, because they lie above the measured vacuum energy. At lower temperature the mobility of the Ag atoms is reduced, and a change of the growth mode to three-dimensional islands occurs, as sketched at the bottom of Fig. 11. The intensity ratio of the peaks corresponding to different layer heights follows roughly the Poisson distribution expected for the case of negligible interlayer mass transport.\textsuperscript{14}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure11.png}
\caption{Two-photon photoemission spectra for 1.0 ML Ag deposited at 90 K on Pd(111) and after heating to the indicated temperatures for 60 s.}
\end{figure}
Figure 12: Vacuum level (solid line) and energies of the detected image states relative to $E_F$ (open symbols) after annealing of Ag films on Pd(111) to 673 K. The short lines show the result of a calculation for a homogeneous surface alloy. Dashed lines give the corresponding quantities for films as deposited at 300 K (compare to Fig. 10).

After heating the sample for 60 s to the temperatures given in Fig. 11 the spectra show pronounced changes. The sample was cooled down to 90 K after the annealing in order to avoid further diffusion during the measurements. The series at lower energies has disappeared after heating just above room temperature. Only electrons from one-layer-thick Ag areas are observed as for the spectrum for 1.0 ML of Ag deposited at room temperature (compare to Fig. 9). The Ag atoms have covered the open Pd(111) patches and the Ag film forms a smooth layer.

For heating temperatures above 500 K the image state shifts to higher energy and becomes broader. At about 600 K one narrow peak is observed, which does not shift in energy up to about 750 K. Its narrow symmetric lineshape is characteristic for an image state on a homogeneous surface. The data shown in Fig. 12 for different coverages annealed to 673 K indicate the formation of a surface alloy, because the energy is always between the values for the completed monolayers (dashed lines). The observed energies can be explained by model calculations\textsuperscript{2,5} and correspond to binding energies similar to the ones for the completed monolayers. A monolayer confined mixing has been found for Ag on Pt(111) at similar temperatures.\textsuperscript{17,18}

For annealing temperatures above 750 K the image state shifts further in the direction of the clean Pd(111) surface. The Ag evaporates or gets incorporated deeper into the bulk. At about 1200 K the image states and the work function of the clean Pd(111) surface are observed.\textsuperscript{14}
4.4. Islands

The concept of the local work function applied to the data for Ag on Pd(111) showed that the image-state series for the bare Pd substrate and Ag layers of different heights have different energies. The assignment of electrons to patches of different Ag coverage implies a lateral localization on a particular island on the surface. The following questions arise: What is the smallest island which can support image states and which effects of the lateral localization can be observed?

The experimental answer to these questions requires the preparation of small Ag islands. This can be achieved by deposition of small coverages at low temperatures where diffusion is reduced. Spectra for Ag coverages between 0.25 and 0.7 ML deposited at 90 K are shown in the left panel of Fig. 13. Compared to the case of a smooth 1 ML Ag film (top spectrum and dashed line in Fig. 13) a shift of more

![Figure 13: Two-photon photoemission spectra for various amounts of Ag on Pd(111) deposited at 90 K compared to an annealed smooth monolayer film. The energy shift (dotted line) and the wave function for an image state localized on a small Ag island is shown at the top right. From the experimental data island size distributions are derived.](image-url)
than 0.2 eV to higher energy is observed. The largest shift and linewidth is observed for the lowest coverage. The lineshape is asymmetric with a tail at the high-energy side. No intensity is seen to the left of the peak excluding any significant occupation of two-layer-high islands.

The energy shifts can be explained by the lateral confinement of the image-state electrons in the potential well of the Ag islands as illustrated at the top right of Fig. 13. The energy boundaries of the potential well are given by the energies of the \( n = 1 \) image state for one layer of Ag on Pd(111) and for clean Pd(111) respectively. This choice of the parameters for the potential well with a depth of 0.76 eV yields the correct limiting values for vanishing and infinite island diameter \( d \). The energy of a particle in a square infinitely-high box of area \( d^2 \) is

\[
\Delta E = \frac{2\hbar^2 \pi^2}{2md^2}.
\]

Other island shapes and potential wells of finite height alter mainly the proportionality factor in Eq. 4 (for energies not too close to the top of the well). The energy shift for localization in one dimension on a stripe of width \( d \) is half the value given in Eq. 4. This implies that Eq. 4 holds within a factor of the order of two even for islands of fractal or ramified shape as observed by scanning tunneling microscopy.\(^{20,21}\)

Equation 4 relates the energy shift to the island diameter and the shape of the spectra in Fig. 13, consequently, reflects the frequency of island areas. The distribution of the islands sizes has been obtained from the experimental spectra using a least-square-fit procedure assuming round islands of finite potential depth.\(^{19}\) The resulting distributions of the coverages by islands of various diameters are shown in the right panel of Fig. 13. The solid lines in the left panel show the fits of the model to the experimental data. The onset of the distributions at \( \approx 10 \) Å diameter is determined by the energy range of the experimental data. The area under each curve is proportional to the coverage. For the data at 90 K the height of the distributions is almost independent of coverage and the mean area of the islands grows proportionally to the coverage.\(^{19}\) This is consistent with a constant density of nucleation centers of \( 7 \times 10^{12} \) cm\(^{-2} \) in the coverage range studied here. This value depends on the experimental conditions such as evaporation rate and temperature and corresponds to a diffusion length of \( \approx 20 \) Å in agreement with work on similar systems.\(^{20,21}\) The width of the distributions increases also with coverage in agreement with the scaling behavior predicted by nucleation theory and monte-carlo simulations.\(^{2,22}\)
5. Conclusions

The examples in this work have illustrated how image states can be used to probe the properties of metal surfaces. For clean surfaces information on the bulk-band gaps is obtained. The quantum well of an overlayer can modify the image states considerably. The concept of the local work function leads to an assignment of electrons to islands of different heights. This permits the study of the growth mode and morphology of thin films. Image states are intrinsic to metal surfaces. They interact only weakly with the electronic states of the sample and are not involved in any bonding. For the experimental investigation of image states a technique with high energy resolution and low background is provided by two-photon photoemission. These methods constitute a unique possibility to study the morphology of surfaces and the growth of thin films through the spectroscopy of electronic states.

Most of the results presented here are from the excellent work of R. Fischer. Additional contributions came from N. Fischer, Chr. Reuß, S. Schuppler, and W. Wallauer. I thank my students and Professor W. Steinmann for the companionship and support in pursuing the endeavor of two-photon photoemission. This work has been supported by the Deutsche Forschungsgemeinschaft (SFB 338).
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