IMAGE STATES OF Ag ON Au(111)

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The image states for thin Ag layers on Au(111) have been studied with two-photon photoemission. The energies of the states show the behavior characteristic for a layer-by-layer growth of large terraces with their characteristic local work function. Image states with rather large linewidths are observed at energies outside the band gap of the projected bulk band structure. The identification of the states is complicated by the dominating signal from the occupied surface state.

1. Introduction

Bound states in front of metal surfaces can exist in the potential well built by the long-range image potential and the band gaps of the projected bulk band structure.1 These states have been detected on low-index single-crystal surfaces by inverse photoemission2,3 and later by two-photon photoemission.4 With inverse photoemission such states have been observed outside the band gap of the projected bulk band structure for Au(111).5,6 Two-photon photoemission results have been obtained so far only for Au films with (111) orientation on different substrates7,8 which are influenced in part by reflection effects in the quantum well of the Au overlayer.7

One aim of this study was to obtain two-photon photoemission results on the (111) surface of a Au single crystal. This system is of particular interest, because there exists also an occupied surface state.9 It may be also observed in the two-photon photoemission spectra and should lead to an enhanced intensity at photon energies where resonant excitation into the image state is possible.4,10,11 From this, information on the lineshapes of two-photon photoemission spectra for on- and off-resonant excitation and their relation to the intrinsic linewidth of the states can be obtained.

When Ag is deposited on Au(111) at room temperature a layer-by-layer growth has been reported.12,13 Both Ag and Au are noble metals with fcc crystal structure and they have almost identical lattice constants. This system, therefore, is ideally suited for studying the electronic states as a function of layer thickness and minimizes unpredictable influences by structural changes due to the accommodation of the lattice mismatch.12,14 On Ag(111), an occupied surface state exists25 and the lowest image state has an energy just at the upper edge of the band gap of the projected bulk band structure.4 It is, therefore, interesting to follow the energies and the linewidths for on- as well as off-resonant excitation of the states as a function of Ag coverage.

2. Experiment

The energy diagram of the two-photon photoemission process is shown in Fig. 1. The frequency-doubled wave of photon energy 2hv is used to excite an electron out of an occupied initial state $E_i$ below the Fermi energy $E_F$ into an intermediate state $E_{in}$. The fundamental wave of energy $hv$ has considerably larger intensity, as indicated by the width of the arrows, and is used to lift the electron into the final state $E_f$ above the vacuum level $E_{vac}$. The electron
The experimental setup used for this investigation has been described in detail elsewhere. An excimer-pumped dye laser is used as a tunable light source in the visible range to produce the ionization pulses of energy $h\nu$ with a duration of 20 ns. A barium-$\beta$-borate crystal produces the pump pulse of energy $2h\nu$, which is perpendicularly polarized to the ionization pulse. The intensity ratio of the two collinear pulses can be varied by a polarizer. A second polarizer turns the polarization of the light into the plane of incidence defined by the surface normal and the light coming in at an angle of 45°. The energy distribution of the emitted photoelectrons is measured with a 160° hemispherical electrostatic analyzer. All spectra shown were measured in normal emission with an acceptance angle of 0.6°, and an energy resolution of about 45 meV has been chosen. The work function $\Phi = E_{\text{vac}} - E_F$ was determined using the known work function of the energy analyzer which was calibrated by the width of photoelectron spectra. Energies of image or surface states and the work function are reproducible to better than 0.03 eV. An argon discharge lamp emitting the main line at 11.83 eV was employed for conventional (one-photon) photoemission measurements. All data were obtained at room temperature, unless stated otherwise.

The Au(111) single crystal was prepared by repeated cycles of Ar⁺ sputtering and annealing to 450°C and additional oxygen exposure to remove carbon. The Au(111) surface showed the $2 \times \sqrt{3}$ reconstruction in the low-energy electron diffraction pattern. This indicates a well-ordered surface. The impurities were below the detection limit in the Auger electron spectra. The sample was kept during the experiments in ultrahigh vacuum at a pressure < 1·10⁻⁸ Pa.

Silver was deposited at room temperature from a resistively heated tungsten basket at a rate of 0.25 monolayers (ML) per minute. The deposited amount of Ag was controlled with a water-cooled quartz microbalance. The first Ag layer grows pseudomorphically on Au(111), showing no reconstruction. The coverage was calibrated using the occupied surface state of the Au(111) surface. The disappearance of this state in the photoemission spectra indicates the completion of the first Ag layer (see Fig. 3). The intensity ratio of the Au and Ag Auger electron lines at 69 eV and 356 eV,
respectively, exhibits changes of the slopes at the monolayer coverages. The work function shows a similar behavior (see Fig. 3). All these coverage calibrations agree and are consistent with the results from previous work on other systems using the same equipment.⁸

3. **Clean Au(111) Surface**

Two spectra for the clean Au(111) surface are shown at the bottom of Fig. 2. The spectra are normalized to the same height and therefore intensities cannot be compared. The energy scale is referred to the Fermi level $E_F$ and applies only to unoccupied intermediate states ionized with photon energy $h\nu$ given at the left of each spectrum in Fig. 2. On this scale the position of intermediate states is independent of photon energy. Consequently, the peak at 4.75 eV must be the $n = 1$ image state which is visible only as a broad shoulder in the spectrum taken with $h\nu = 2.48$ eV. This value is in agreement with results from inverse photoemission on Au(111)⁵,⁶ and two-photon photoemission on Au films of (111) orientation.⁷,⁸ With the value of 5.55 eV for the work function of the clean Au(111) surface this leads to a binding energy of the first image state relative to $E_{\text{vac}}$ of 0.80 eV. This is in moderate agreement with calculated values of 0.85 eV,⁸ 0.87 eV¹⁶ and 0.68 eV.¹⁹ A signal attributable to the $n = 2$ state has not been observed. The expected energy of the $n = 2$ state is $\sim 0.2$ eV below $E_{\text{vac}}$, and there are no initial states available for photon energies below the work function. A similar situation exists for Cu(111).¹⁰ The $n = 1$ image state on Au(111) is hardly visible in the two-photon photoemission spectra compared to the signal from the occupied surface state discussed below. This can be explained by its position outside the band gap of the projected bulk band structure extending from $-1.0$ to $3.6$ eV.⁶ The image state is degenerate with bulk states, which provides an efficient channel for decay.¹⁷ The resulting short lifetime of the state leads to a large intrinsic linewidth of $160 \pm 40$ meV.¹⁶ Calculations of the density of states for the $n = 1$ image state on Au(111) show a peak width of $\sim 200$ meV.¹⁹

The dominant peak in the spectrum taken at 2.48 eV is assigned to the occupied surface state of Au(111). The correct energy for this state is obtained after subtracting $2h\nu$ from the energy read off in Fig. 2. We obtain a value of 0.41 eV below $E_F$, in agreement with our one-photon photoemission experiments and previous reports.²⁰-²² For 2.58 eV the photon energy $2h\nu$ equals the energy difference between the occupied surface state and the image state. Therefore, only one peak is observed in the bottom spectrum of Fig. 2. For Au(111) no resonant enhancement of the intensity could be identified, in contrast to similar fcc(111) surfaces.⁴,¹⁰,¹¹ The excitation from the occupied surface states via intermediate bulk states seems to be as efficient as via the first image state. The latter is degenerate with the bulk states and has a large penetration into the bulk. The matrix element for optical excitations is dominated by the overlap of the wave function in the bulk. Even for an occupied surface state the wave function has decayed at the distance where the wave
function of the first image state has its maximum. This makes the absence of a strong resonance effect plausible in the present case of an image state in a continuum of bulk states.

One-photon photoemission experiments at 90 K show a downward energy shift of 0.04 eV for the occupied surface state, in agreement with the literature. This behavior is found also in the two-photon photoemission spectra, where a lower energy is observed for the peaks assigned to the occupied surface state at 90 K compared to the data obtained at room temperature. The linewidth decreases also with temperature from 135 meV [full width at half maximum, (FWHM)] at 300 K down to 90 meV at 90 K. This effect is observed in one- as well as two-photon photoemission data. The larger peak widths measured by Paniago et al. might be attributable to some extent to the higher photon energy and lower angular resolution used, but more likely to a poorer quality of the Au(111) surface.

4. Ag/Au(111)

Two-photon photoemission spectra for Ag coverages up to 3.2 ML are shown in Fig. 2. For the Ag-covered surface the dominant peaks correspond to resonant transitions between the occupied surface state and the image states. This has been verified from the photon energy dependence of the peaks. Independently, one-photon photoemission measurements prove the existence of the occupied surface state over the entire coverage range and give the energy of the state below $E_F$. With the known photon energy the position of transitions from the occupied surface state in the spectra of Fig. 2 can be determined and the resonance be verified. It is interesting to note that a resonance effect in the intensity is observed for the second layer of Ag. This can be seen in the spectra for 1.9 ML from the strong intensity of the $n = 2$ image state around 4.4 eV compared to that of the $n = 1$ image state around 3.9 eV. The resonance with the occupied surface state is observed for the $n = 1$ image state at 2.07 eV photon energy and for the $n = 2$ state at 2.33 eV. The drastic changes of the relative intensity of the members of the image state series are typical for resonant excitations from occupied surface states. An exception occurs for the clean Au(111) surface where no resonant intensity enhancement could be identified (see Sec. 3). The spectra of Fig. 2 show differences in the width of the peaks depending on coverage and even more pronounced changes depending on the photon energy at fixed coverage. This will be discussed in more detail in Sec. 5.

For a more detailed understanding of the behavior of the surface and image states, the results from many measurements for the energies are plotted in Fig. 3 as a function of Ag coverage. The lower part of Fig. 3 shows the energetic position of the occupied surface states which are observed throughout the entire coverage regime. The state at $-0.41$ eV characteristic for the Au(111) surface disappears at 1 ML, whereas a new state at $-0.27$ eV appears already.

![Fig. 3. Energies of image states $n = 1$ and $n = 2$ and occupied surface state $n = 0$ as a function of Ag coverage on Au(111). Average values of the image states are shown by the horizontal lines. As symbolized by a line the vacuum energy $E_{vac}$ decreases linearly between the completed layers.](image-url)
Table I. Work function $\Phi$ and energies of the occupied surface state ($n = 0$) and the lowest image states for the clean Au(111) surface and Ag films on Au(111). The data are given in eV relative to the Fermi level $E_F$ and have a typical error of 0.03 eV. The experimental data are compared to the results of a calculation with a one-dimensional scattering model\textsuperscript{30} for two different values of the imaginary part of the potential $V_i$.  

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at a coverage < 0.2 ML. For coverages up to 1 ML, $n = 0$ states on the clean Au(111) terraces and on one-layer high Ag islands are resolved separately, in contrast to previous studies\textsuperscript{25-27}. This behavior is in agreement with the layer-by-layer growth for the first Ag layer.\textsuperscript{13} The disappearance of the Au(111) state can be used for the coverage calibration (see Sec. 2). The state on the silver islands shifts for coverages above 1 ML only slightly in energy at a rate of 0.04 eV/ML and reaches the asymptotic value of $-0.05$ eV typical for the Ag(111) surface state\textsuperscript{4,21,22} around 20 ML. For coverages above 4 ML, quantum well states were observed in the energy range between $-1.5$ eV and $-0.4$ eV, in agreement with other investigations.\textsuperscript{26,27} In this energy range the Ag overlayer forms a quantum well, because there are no allowed states at the vacuum as well as the Au(111) side. The Ag overlayer offers states in the projected bulk band structure with the band gap extending from $0.31$ eV to 3.09 eV.\textsuperscript{28}

The vacuum energy $E_{vac}$ is shown as a solid line because the scatter of the data points is comparable to the size of the symbols in Fig. 3. The line for the vacuum energy shows pronounced changes in slope at coverages of 1 and 2 ML. This is in agreement with the layer-by-layer growth for the first Ag layers.\textsuperscript{12,13} The vacuum energy gets close to the asymptotic value of 4.59 eV characteristic for Ag(111)\textsuperscript{4} already for 3 ML. Most of the change occurs during the initial decrease from 5.55 eV for the clean Au(111) surface to 4.97 eV for the first monolayer. A similar behavior has been found for Ag on Pd(111).\textsuperscript{29}

The unoccupied image states are observed in a certain coverage range without changing their energy relative to $E_F$ significantly. This contradicts the expectation that the image state series converges towards the vacuum level which is the asymptotic limit of the image potential. The problem can be solved if one assumes that the image states are pinned to the vacuum level of the individual patch which they are located on.\textsuperscript{20} This picture is correct if the lateral extension of the terraces or islands is large compared to the distance of the electron in the image state from the surface.\textsuperscript{31} The local vacuum level is identical to the average macroscopic vacuum level measured far away from the surface only for completed layers, when the Ag overlayer has a homogenous thickness. Indeed, the states at 4.23 eV and 3.91 eV have binding energies typical for $n = 1$ image states, when one is calculating the binding energies relative to the vacuum levels for 1 and 2 ML, respectively. The assignment to $n = 1$ image states is confirmed by the observation of the second member ($n = 2$) of the series of image states for coverages above 1.7 ML (see Fig. 3) and by the observed sharpness of the peaks in Fig. 2 indicating a long lifetime of these states.
typical for image states. The fact that the $n = 1$ image state of the one-layer-thick areas at 4.23 eV is observed only between 0.2 and 1.8 ML and that the $n = 1$ image state of two-layer-thick areas is observed at 1.1 ML and higher coverages confirms the layer-by-layer growth up to a coverage of 2 ML. The image states reach the energy known for the Ag(111) surface within the error limits for coverages above 3 ML. This is in qualitative agreement with the results for the similar system Ag/Pd(111), for which an exponential decay of the energy on the scale of 3.2 ML has been found. The energies of the surface states were calculated using a one-dimensional scattering model. Experimental input parameters have been quoted earlier. The band structure parameters were the measured work function for the completed monolayer coverages of Ag on Au(111). The results of the calculations are compared in Table I to the experimental data. The agreement is quite good, if an imaginary part of the potential $V_i$ is included. This leads to a finite penetration of the wave function into the bulk also for energies outside the band gap, as is the case for Au(111). The agreement for the occupied surface state is slightly worse, because of the poor treatment of the potential in this energy range.

5. Linewidth

The behavior of the energies of the image states as a function of Ag coverage on Au(111) is similar to previously studied systems. The main difference is the large linewidth of the image state on Au(111), as discussed already in Sec. 3. Taking a look at Fig. 2, one recognizes that also for the Ag films the width of a peak is different for resonant and nonresonant excitation. The off-resonant spectrum of the two-layer peak at 3.91 eV taken at a photon energy of 2.23 and 2.33 eV is much broader than the corresponding peak taken at the resonant photon energy of 2.07 eV. For further consideration the FWHM of the $n = 1$ and $n = 0$ states in resonant and nonresonant two-photon photoemission spectra is shown in Fig. 4 as a function of Ag coverage. With the exception of the image states on 1 ML Ag, the FWHM of the $n = 0$ states is slightly larger than the FWHM of the resonant $n = 1$ spectrum. Obviously the two-photon photoemission process is influenced by the choice of the initial state. A dominant influence on the spectra by the initial state is explained in the following model. The probability for the second-order process is given by the product of the spectral densities of the initial and the intermediate state as suggested in Fig. 1. This yields a narrower linewidth for resonant excitation than observed for both contributions off-resonance.

For a more accurate determination of the widths of the peaks we performed line fits to the experimental data. One-photon photoemission spectra ($n = 0$) and off-resonant two-photon photoemission spectra ($n = 0$ and $n = 1$) were fitted by a convolution of a Lorentzian representing the intrinsic linewidth of the states with a Gaussian representing the experimental energy resolution of 45 meV. The FWHM is determined mainly by the experimental data and depends only weakly on the partitioning between the Lorentzian and Gaussian contributions. For the resonant spectra a product of two Lorentzians using the previously determined intrinsic linewidth for the $n = 0$ and $n = 1$ states was convoluted with a

![Fig. 4. Full width at half maximum of the peaks as a function of Ag coverage. The data for $n = 1$ state (filled diamonds) and for resonant excitation (filled squares) are from two-photon photoemission spectra, whereas the data for the $n = 0$ surface state (open circles) are from one- and two-photon photoemission spectra.](image-url)
Gaussian. The Gaussian resulting from the fit has a width between 40 and 50 meV, close to the chosen experimental resolution. The only exception is the $n = 1$ state of one-layer-thick areas where the fitting procedure leads to a Gaussian of about 90 meV. The fit with the product of two Lorentzians leads to a slightly better fit of the resonant spectrum than a fit with a single Lorentzian. However, the FWHM plotted in Fig. 4 is hardly influenced by the fit function. The main advantage of this model function for the resonant spectra is the physically meaningful widths of contributions to the fit function. For the data shown in Fig. 4 the resonant linewidth is only slightly smaller than the width of the $n = 0$ initial state, because the image state has a large intrinsic linewidth. The effect is much more pronounced when both states have a similar linewidth as in the case of the Cu(111) surface. For this system an intrinsic linewidth of 16 meV has been determined in resonance. A recent analysis assuming the product of the spectral densities gave an intrinsic linewidth of 85 meV for the image state.

For one-layer-thick films the linewidth involving the $n = 1$ image state is larger than expected (see Fig. 4). The fits of the spectra yield a Gaussian contribution considerably larger than the experimental resolution. In addition, the poorest agreement between experiment and calculation for the first image state in Table I is found for 1 ML Ag on Au(111). These observations seem to contradict the pseudomorphic layer-by-layer growth found in structural studies. Our two-photon photoemission results indicate an inhomogeneous surface with small patches of different local work functions. A possible explanation could be the incorporation of the extra Au atoms of the $22 \times \sqrt{3}$ reconstructed Au(111) surface into the first Ag layer which lifts the reconstruction. Further structural studies are needed to clarify this question.

6. Summary

The energies of the image states for thin layers of Ag on Au(111) show the behavior expected for a layer-by-layer growth within the model of the local work function. The results show that image states can be observed with two-photon photoemission even when they are located energetically outside the band gap of the projected bulk band structure. The large intrinsic linewidth is connected with a short lifetime and makes the observation of the states rather difficult. Special care has to be taken to identify the image states from the dominant signal of the occupied surface state and to obtain the correct photon energy for resonant excitation.

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References