Spin-resolved photoemission from epitaxial Au layers on Pt(111): coverage dependence of the bandstructure and evidence of surface resonances

B. Vogt, B. Schmiedeskamp, and U. Heinzmann

Universität Bielefeld, Fakultät für Physik, D-4800 Bielefeld 1, Federal Republic of Germany
and Fritz-Haber-Institut der Max Planck Gesellschaft, Faradayweg 4–6, D-1000 Berlin 33, Germany

Au/Pt(111) has been studied by spin-, angle- and energy-resolved photoemission with normal incident circularly polarized synchrotron radiation of BESSY and normal photoelectron emission for different Au coverages. The prepared layers were characterized by LEED and Auger-electron spectroscopy and turned out to grow up two dimensional and epitaxially. In the photoemission experiments the development of the 3-dimensional bandstructure in the Λ-direction could be observed. For a coverage of 2.6 layers the highest occupied spin-orbit split bands are located at about 0.6 eV lower binding energy than the corresponding bands for a $3D$-Au crystal and show dispersion which is, however, weaker than in a $3D$-Au crystal. A 5 layer Au adsorbate was found to have already the same dispersion and energetic location as a Au(111)-crystal. For thick gold layers, which behave in photoemission like Au(111)-crystals, we find structures that cannot be due to direct transitions into a free electron like final band. The coverage dependence and spin polarization of these structures show that some of them are due to surface resonances, while the origin of one strong peak could not yet be explained conclusively. In addition we find strong hybridization and two avoided crossings in the occupied part of the bandstructure.

Introduction

The adsorbate system Au/Pt(111) has already been studied by different experimental methods. With TDS, Auger-electron spectroscopy (AES) and LEED information about the adsorption of Au on several Pt surfaces including the (111)-surface could be obtained [1]. Photoemission studies have been performed on Au/Pt(111) for different Au coverages [2]. HeI radiation and an almost integral electron analysis was used in [2]. Angle and energy resolved studies with synchrotron radiation (i.e. with photon energy variation in the VUV range) have up to now been performed with Au(111) [3 and

references therein] and Pt(111) [4, 5, 6] single crystals. Even more elaborate and powerful is this experimental tool if in addition the photoelectron spin polarization is analyzed [4, 5, 7–14]. In [4] and [5] the photoelectron spin analysis allowed a symmetry resolved mapping of the valence bands of Pt(111) in the Λ-direction and in [7–14] information about hybridization and avoided crossings was obtained for example at other targets than Pt(111).

In the present work we apply the spin-, angle- and energy-resolved photoemission with circularly polarized synchrotron radiation to the adsorbate system Au/Pt(111) for different Au coverages. These studies supplement the previous work [2, 3] and yield information regarding to several unanswered questions.

One of these questions regards puzzling dispersionless features D_1, D_2 and D_3 which could not be unambiguously identified in [3] and were tentatively interpreted as surface resonances. We use the sign of the spin polarization and the coverage dependence of these structures in order to get strong hints regarding their nature.

Another question concerns the occupied part of the Au-bulk bandstructure in the Λ-direction. Does a crossing point of the first two bands, $A_{4,5}^3$ and A_6^1, below E_F exist or not? Theory [15] predicts a crossing point while non spin resolved photoemission data [3] do not seem to indicate such a crossing. Spin-resolved photoemission should help to answer this question.

In a high Z material as gold hybridization will play an important role. Crossings of A_6^1 and A_6^3 bands are avoided and yield extended parts of the bands containing both A^3- and A^1-spatial parts of the Bloch spinors. Information about both the degree of hybridization and the occurence of crossings and avoided crossings can be obtained from the spin polarized photoemission studies [7–14]. In addition (especially also to the work in [2]) we can also measure $K_\perp$-band dispersions vs. coverage and, especially, Au coverage dependent spin-orbit splittings. Information about the development in the unoccupied part of the Au-bandstructure is obtained from the resonant behaviour of peaks at about 4.7 and 6 eV below

E_F which (for the Au(111)-crystal) arise from transitions into a crossing region of two Λ_6^1 final bands.

In a recent work on epitaxial Ag layers on Pt(111) [7] a peak in the spin resolved photoemission spectra was found to contribute to the resonances which is not predicted by existing theoretical models [3, 16]. A corresponding peak for Au is studied in this work.

Experimental

The experiments were performed at the 6.5 m normal incidence VUV-monochromator [17] at BESSY with circularly polarized off-plane radiation. The apparatus used for the measurements has been described in general [4], in addition an evaporator was integrated.

All photoemission data were obtained for normal incidence of the circularly polarized radiation and normal emission of the photoelectrons. The photoelectrons were analyzed with respect to their kinetic energy and emission angle by an electron spectrometer [18]. The overall energetic resolution (electrons plus photons) was better than 200 meV at an angular resolution of ± 3° (geometric resolution).

The surface normal of the Pt(111) crystal coincided within 0.5° with the [111]-direction and within 0.3° with the light direction. The clean crystal surface was prepared by cycles of Ar$^+$- and Ne$^+$-bombardment, heating in oxygen, and flashing. It was controlled by Auger-electron spectroscopy (AES) and LEED.

The evaporation was performed with the substrate at room temperature with a resistively heated Au evaporator. It was placed ≈ 20 cm away from the target. The Au beam was collimated by a small tube. After an initial outgazing the evaporator worked without strong influence onto the UHV-conditions (base pressure in the 10^{-10} mbar range). It was used for short periods, between them the surface was controlled by LEED and AES.

Results and discussion

AES and LEED was also used to determine the growth of the deposits. While the LEED spots did not show changes in geometry during the evaporation time up to the coverage of a thick Au layer, the Auger signal of Pt and Au decrease and increase, respectively, rapid with evaporation time. In agreement and analogy with [2, 19] we find that Au grows 2-dimensional and epitaxially.

The coverage calibration was performed by a direct comparison of the AST-plot and the Auger spectra itself with those in [19]. Due to the Pt and Au superposition the Auger spectra are very sensitive to the coverage in the monolayer regime. In addition the absolute coverage of one layer Au was determined in an independent way by calibrating the evaporator by means of an AST-plot of Au/Si(111) [20].

Another information received from the LEED studies is that the energy dependence of the LEED pattern shows the three brighter spots of the thick Au layer at
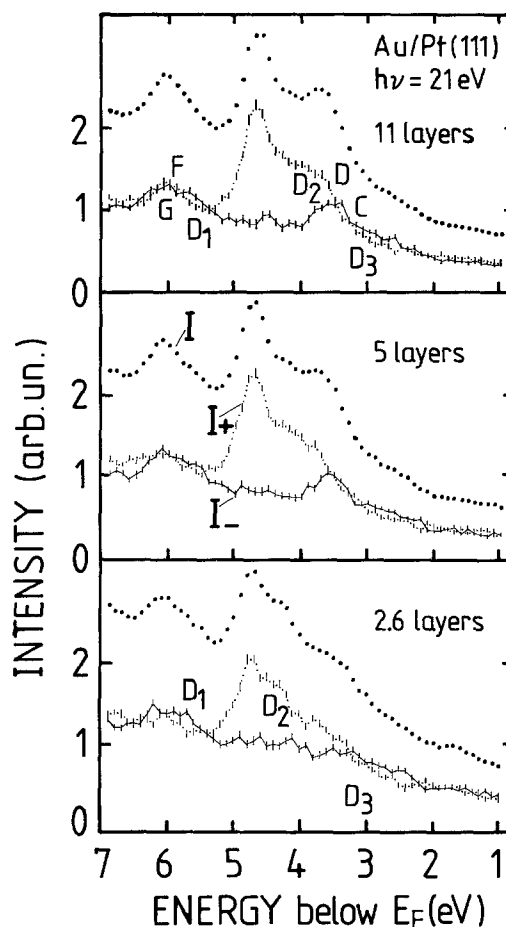

Fig. 1. Photoemission spectra of Au/Pt(111) for different coverages from 2.6 up to 11 layers at $h\nu = 21$ eV. The total intensity is marked by dots, the partial intensities I_+ and I_- are marked by dashed and solid lines, respectively. The error bars represent the total error including the statistical error of the count rates and the uncertainties of the light polarization and of the detector asymmetry function

the positions of the three darker spots of Pt(111). This favours a Au growth starting on hcp places.

The Au layers prepared in this way were studied with spin-resolved photoemission for different coverages and photon energies. Photoemission spectra for 21 eV photon energy and different Au coverages are given in Fig. 1. In each part of the figure the total photoelectron intensity I (dotted curve) is given and separated into the partial intensity I_+ (dashed curve) and I_- (solid curve) by means of the spin polarization P according to

$$I_+ = \frac{I}{2}(1+P) \quad \text{and} \quad I_- = \frac{I}{2}(1-P).$$

I_+ denotes the intensity of the photoelectrons with spin parallel to the photon spin, I_- the intensity of photoelectrons with the opposite spin direction.

Concerning the development of the spectra in Fig. 1 with coverage we note a considerable change in the shape of the spectra when going from a 2.6 layer Au adsorbate (lower part) to the 5 layer adsorbate (middle part). Almost no change in the spectrum is, however,
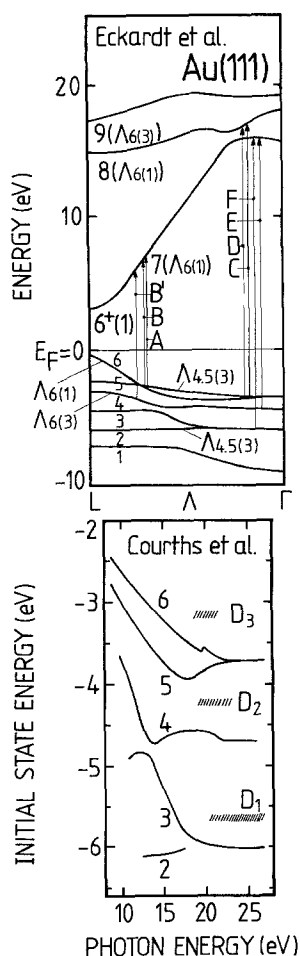
Fig. 2. Upper part: bulk bandstructure of Au in the Λ-direction by Eckhardt et al. [15]. A, B and B' indicate the transitions corresponding to the peaks in the spectra of Fig. 4, C–F indicate the transitions of peaks C–F in Fig. 1. Lower part: Experimental bands of Au in the Λ-direction by Courths et al. [3]; features D_1–D_3 correspond to dispersionless peaks in the photoelectron spectra

We have studied the behavior of these features spin-resolved for different photon energies and two different gold coverages. The results are given in Fig. 3. In the lower part we present the photoemission spectra for a gold coverage of 2.6 layers. The spectra in the upper part were measured for 5 layers Au coverage. As in Fig. 1 the spectra are again given as total intensities I and partial intensities I_+ and I_-. Again all the spectra mainly consist of the peaks labelled C, D, E and F, but the existence and coverage dependence of the features D_1, D_2 and D_3 is now also clearly demonstrated in the spectra. For 21 and 21.5 eV photon energy D_2 is revealed and shown to decrease strongly with coverage compared to the neighbouring peaks. The same behavior is observed for D_1 in the spectra for 22 and 23 eV, while for the weakest of the structures, D_3, we cannot make a definite statement regarding the coverage dependence. We note further that the spin polarization sign of D_2 and D_1 is the same as for the peaks E and F, respectively. Both the decrease of D_1 and D_2 with coverage and the identical spin polarization sign as E and F, respectively, fits into the model that D_2 and D_1 are surface resonances with E and F as the corresponding bulk states.

Another result obtained from Fig. 3 regards the coverage dependence of the direct transitions C and D from band 5 and 6. For lower Au coverage of 2.6 layers peak C seems to be almost completely suppressed while considerable intensity is measured in peak D. This might be due to the development of the three dimensional bandstructure. Band 5 is a $\Lambda_{4,5}^3$ band which is built up of orbitals with spherical symmetry, whereas the Λ_6^3-band consists of orbitals with xy symmetry at the Γ point [21].

A further point of interest in the spectra of Fig. 3 is a positively polarized peak, which is localized very close to peak F and which we denote G. Peak G also shows a resonant behavior with photon energy, it seems to increase with Au coverage and to shift with photon energy slightly towards higher binding energy. This is a behavior similar to that of a corresponding peak G which was observed in a recent work on epitaxial Ag layers on Pt(111) [7]. The Au data provide additional information concerning peak G. For Au peak G is energetically close to peak F in contrast to Ag where peak G lies between the peaks E and F. In this case an explanation that comes in mind is that parts of peak G and peak F arise from a transition that yields spin polarization different from 1. Such a transition can for example occur from the lowest $\Lambda_{4,5}^3$ band (compare Fig. 2) into the short part of the flat f-like unoccupied band very close to Γ (right upper part of band 7). For transition from $\Gamma_{8+}^{25'}$ to Γ_7^{2-} the group theory [22] predicts indeed a spin polarization of -0.5. This can explain the existence of parts of peaks like G but it can neither explain intensities of G larger than one third of the intensity of F (as found for 21 eV and 21.5 eV) nor the strong decrease of G when going from 21.5 eV to 23 eV photon energy. The nature of peak G seems thus to be a still open question.

We return now to Fig. 2 to discuss another point. In the theoretical bandstructure [15] (upper part) there
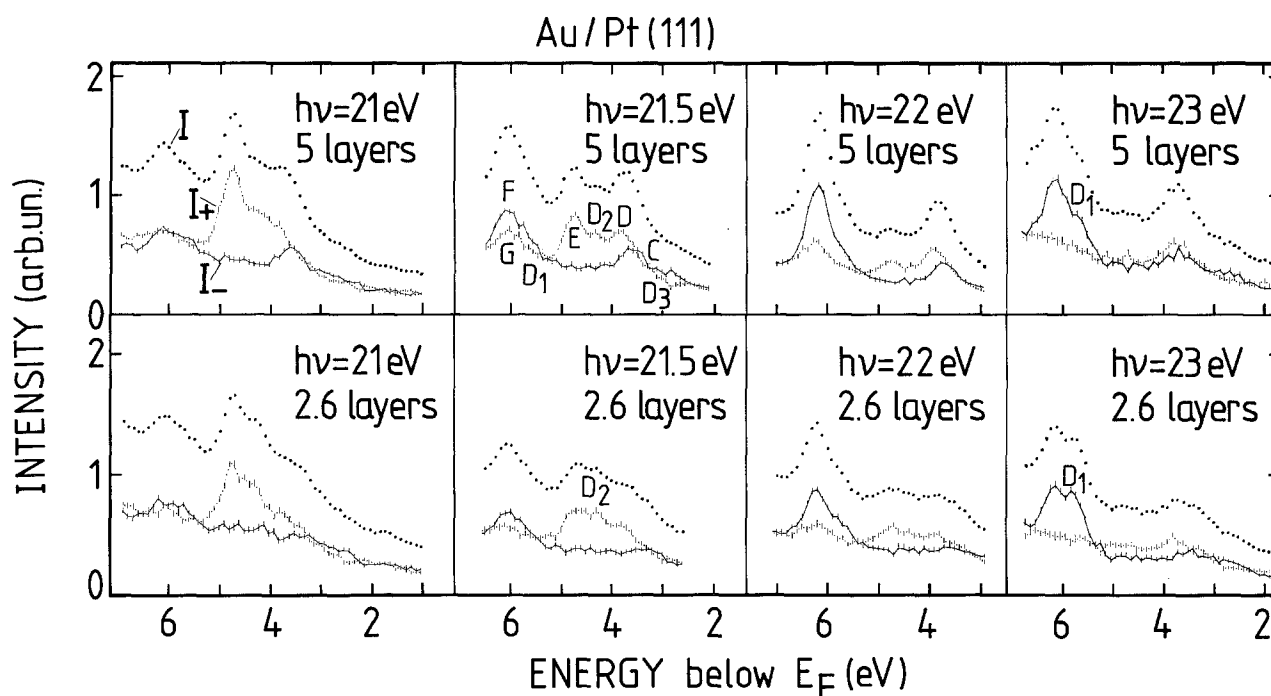
obtained, when the coverage is further increased. In the spectrum for a Au coverage of 11 layers (upper part of Fig. 1) three peaks could be resolved in the non spin resolved intensity (dots). This spectrum agrees well with a spectrum obtained for Au(111) in [3] in peak positions. According to [3] the first peak below E_F is due to two transitions C and D into the free electron like final band. This is illustrated by the arrows in the bulk bandstructure for Au in the Λ-direction in Fig. 2. Arrows labelled E and F in Fig. 2 denote transitions corresponding to the peaks E and F in Fig. 1. Courths et al. [3] studied the photoemission from Au(111) for photon energies around 21 eV in detail and found further dispersionless structures D_1, D_2 and D_3. They should also be visible very weakly in a 21 eV spectrum at the positions indicated in the upper part of Fig. 1. These structures could not be unambiguously identified in [3] and were tentatively interpreted to be surface resonances. Their possible locations in the bandstructure are given in the lower part of Fig. 2 which shows the experimental band mapping data of [3] for Au(111).

Au / Pt (111)

Fig. 3. Photoelectron intensities of Au/Pt(111) for $hv=21$, 21.5, 22 and 23 eV and coverages of 2.6 and 5 layers. The 4 peaks $C-F$ correspond to Au transitions (Pt peaks are suppressed due to a bandgap in the unoccupied part of the Pt bandstructure). The peaks E and F show a stronger increase with coverage than the peaks C and D. Spin polarization reveals a further peak G, which is not predicted by theoretical models for the resonant behavior. Peaks D_1-D_3 seem to correspond to surface resonances

is a crossing point of the two uppermost valence bands 5 and 6. This crossing point should also be visible in the experimental bandstructure [3] in the lower part of Fig. 2. The data seem, however, to indicate no such crossing. Spin-resolved photoemission can distinguish between bands of different symmetry and is thus an ideal tool for the experimental characterization of crossing points [7–14]. Band 5 has $\Lambda_{4,5}^3$ symmetry and yields completely negatively spin polarized electrons (i.e. an electron spin opposite to the photon spin) for transitions into the free electron like final band 7. Band 6 is a $\Lambda_6^3 \Lambda_6^1$ hybrid due to an avoided crossing of a Λ_6^3 band and a Λ_6^1 band and yields positively polarized electrons due to its Λ_6^3 part, since a transition from its Λ_6^1 part into band 7 (also Λ_6^1 symmetry) is dipole forbidden for our experimental geometry (normal incidence of radiation and normal electron emission). The transitions from this crossing part of the valence band structure into band 7 can be observed for photon energies between 8 and 10 eV and yield photoelectrons with kinetic energies only a few eV above the vacuum level. For a photon energy of 9 eV one expects transitions A, B and B', which are given as arrows in Fig. 2 (upper part) i.e. a photoemission spectrum with 3 peaks. Peak A (with the lowest binding energy) should be negatively polarized, peak B and B' are expected to be positively polarized (B' is a transition from band 4, which is also a $\Lambda_6^3 \Lambda_6^1$ band; this band is due to two avoided crossings in the bandstructure). That this is indeed the case can be seen in Fig. 4, in which the spin-resolved photoemission spectra for $hv=8$–9.2 eV are presented. For photon energies above 8.5 eV

we find 3 peaks with the expected spin-polarization sign, 1 eV energy difference in binding energy is found for the peaks B and B' which arise originally from the same Λ_6^3 band. We have thus found that strong hybridization occurs indeed in this part of the bandstructure due to an avoided crossing point. This is further supported by the decrease of the energy splitting of the peaks A and B from 0.25 eV at 9.2 eV to less than 0.1 eV at 8 eV photon energy which indicates both that a crossing point of band 5 and 6 exists indeed and that the hybridization area extends at least up to this crossing point.

The binding energies of the peaks A and B have also been determined for higher photon energies up to 18 eV; they have been found to be in very good agreement with the data of Courths et al. [3] (already given in the lower part of Fig. 2) and show a slight discrepancy with corresponding parts of the calculated bandstructure of Eckhardt et al. [15], which is also given in Fig. 2.

In order to get information about the coverage dependence of the spin-orbit splitting, band dispersion, and binding energy of bands 5 and 6 we have also determined the energetic positions of peaks A and B for two further coverages, 2.6 and 5 layers. They are plotted vs. photon energy in Fig. 5. The results for the 5 layer adsorbate agree quite well with those obtained above for the thick gold layer. For 2.6 Au layers we observe a shift of the bands up to 0.6 eV towards lower binding energy and a slightly decreased band dispersion. The spin-orbit splitting in this part of the bandstructure seems, however, to maintain its value.
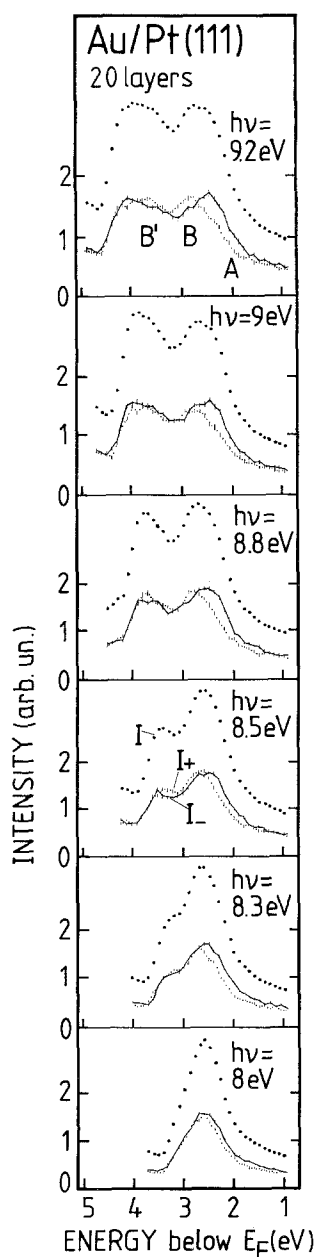
Fig. 4. Photoelectron intensities of Au/Pt(111) for a thick Au-layer for $h\nu = 8$, 8.3, 8.5, 8.8, 9 and 9.2 eV. The peaks A, B and B' correspond to the transitions A, B and B' in Fig. 2
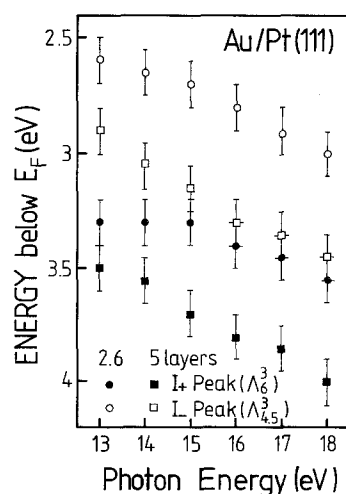

Fig. 5. Energy below E_F vs. photon energy for peaks A and B for coverages of 2.6 and 5 layers

binding energy and a missing peak corresponding to a $\Lambda_{4,5}^3$ initial state for a Au(111) crystal for $h\nu = 21$ eV. Information was also obtained about structures which are not due to bulk transitions into a free electron like final band. Two of these structures are probably due to surface resonances. Further features could be gathered about one strong peak, which contributes to intensity resonances for photon energies between $h\nu = 20$ eV and 24 eV. Evidence for strong hybridization due to an avoided crossing in the occupied part of the bandstructure was found. The data also indicate that a crossing of the first $\Lambda_{4,5}^3$ and Λ_6^1 band below E_F exists.

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Summary

We have examined Au/Pt(111) with spin-resolved photoemission for different Au coverages. Characterization of the prepared layers by AES and LEED showed that Au grows two dimensional and epitaxial on Pt(111). The spin-resolved spectra for thick Au layers agreed completely in energy positions with those of a Au(111) single crystal [3]. Spectra of a 5 layer adsorbate were almost identical with those of thick Au layers, while a 2.6 layer Au adsorbate turned out to yield considerable different spectra: reduced band dispersion, a shift of up to 0.6 eV of the first $\Lambda_{4,5}^3$ and Λ_6^3 bands below E_F towards lower

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