

Au-Induced Surface State on Pt(111) Revealed by Spin-Resolved Photoemission with Linearly Polarized Light

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Photoelectrons ejected by normally incident linearly polarized HeI radiation and emitted normal to epitaxial Au layers on Pt(111) are strongly spin polarized for both emission from the Pt substrate and the Au adsorbate up to 2.2 layers coverage. Relativistic Green's-function calculations reproduce the measured data and reveal the physical origin of the polarization for a monolayer Au coverage to be a Au-induced surface state. The spin polarization is significantly influenced by the underlying Pt bulk and is thus a sensitive measure of the Au adsorption site.

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Contrary to common belief, photoelectrons ejected by normally incident linearly polarized radiation and emitted normally to the surface of a nonferromagnetic centrosymmetric cubic crystal can be spin polarized.^{1,2} The effect was observed in Ref. 2 for transitions into band-gap states, i.e., the effect turned out (as already predicted in Ref. 1) to be surface sensitive.

In the present work this surface effect has been measured and calculated for the first time for an adsorbate system. Au was chosen as adsorbate because it grows two dimensionally and epitaxially on Pt(111) (Refs. 3 and 4) and has a similar electronic structure. This work has two parts. First, it is studied how the spin polarization of the Pt(111) substrate is modified with adsorbate coverage. Second, the spin-polarization effect for photoemission from the Au adsorbate layer itself is measured in order to learn more about its origin and its dependence on surface properties. In addition, the size and sign of the spin polarization depends on the geometric arrangement of substrate and adsorbate atoms. Rutherford-backscattering studies in combination with channeling are done to give information about these geometric arrangements.

The experimental setup is described in principle in Fig. 1. The radiation source is a capillary discharge tube of the type given in Ref. 5. It yields HeI radiation (21.2 eV), which is linearly polarized after reflection at three gold mirrors.⁶ The degree of polarization is 88% ($\pm 4\%$).⁷ The Pt crystal surface coincides better than 0.5° with the (111) plane and is aligned to be within 0.3° of perpendicular to the direction of the incident light. The target preparation includes Ne^+ and Ar^+ bombardment followed by heating in oxygen and annealing at 500°C .

The Au layers are evaporated with a resistively heated Au evaporator. During the evaporation the target is held at room temperature. The evaporation process is interrupted for AES (Auger-electron spectroscopy) and

LEED (low-energy electron deflection) to control the growth of the layers. The thickness of the respective Au layers is determined from an Auger signal versus time plot (AST plot). This AST plot in connection with LEED suggests two-dimensional epitaxial growth in accordance with measurements of other authors.^{3,4}

The photoelectrons emitted normal to the surface within an angular cone of $\pm 3^\circ$ are detected in a simulated hemispherical electron spectrometer.⁸ The adjusted energy resolution of the spectrometer is approximately 400 meV. The spin analysis is performed by Mott scattering at 100 keV. In the Mott detector two components of the spin-polarization vector \mathbf{P} are detected simultaneously. One component (P_y) is parallel to the crystal surface, and the other (P_z) parallel to the surface normal.

The photoemission is performed for normal incidence of the linearly polarized radiation. Rotation of the Pt sample by ω about the surface normal induces a sinu-

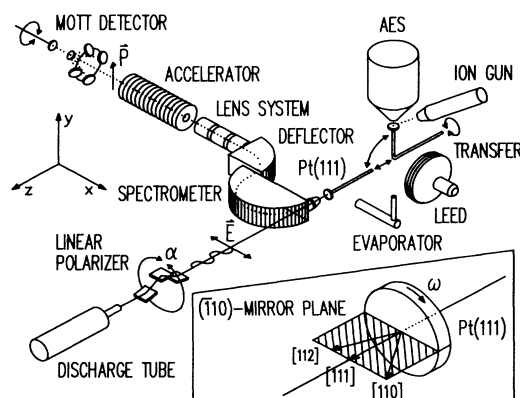


FIG. 1. Experimental setup: Spin-resolved photoemission with normally incident and linearly polarized radiation and with normal electron emission.

soidal variation of P_y , which is compatible with a rotation of the spin-polarization vector \mathbf{P} by 3ω in the x - y plane [$\text{by } 2\omega$ in the frame fixed to the crystal (Fig. 1 in Ref. 1)]. Rutherford backscattering in combination with channeling is applied to determine a relation between the orientation of the spin-polarization vector and the stacking sequence in the clean Pt(111) crystal. P_y turns out to be positive and a maximum if the \mathbf{E} vector of the incident radiation is parallel to both the x axis and the $(\bar{1}10)$ -mirror plane, as oriented in Fig. 1. All photoemission spectra displayed in the present work are obtained for this special experimental arrangement and thus the obtained P_y values are denoted as P in the following. P_z remains zero during all sample rotations about the surface normal. This shows that there is no spin polarization in the z direction which might be yielded by a circularly polarized radiation component.³

The relativistic photoemission theory, which we have previously developed and applied (Refs. 1 and 9, and references therein), has been generalized in the following two respects. First, the Bloch-wave construction of the initial state has been replaced by a Green's-function treatment, which is essentially a relativistic generalization of Pendry's¹⁰ dynamical method. This allows not only an *a priori* incorporation of the hole imaginary self-energy part, but also automatically includes initial states which are localized in the surface region (surface states). Second, the method has been extended to the case of a commensurate adsorbate layer on the semi-infinite substrate. We can thus study emission from adsorbate-induced surface states and resonances.

Our computer code was accordingly modified. Extensive vectorization reduced the computing time per energy point (on a CRAY-YMP computer) to about 0.9 sec for a clean Pt(111) surface and to 1.2 sec with an adsorbed Au layer. Calculations of intensity and spin-polarization spectra from clean Pt(111) by circularly and linearly polarized light identically reproduced our earlier results.¹ Apart from serving as a program check, this demonstrates the adequacy of our earlier method for the case of bulk interband transitions.

In view of interpreting photoemission spectra, we simultaneously calculate for the adsorbate system under consideration the underlying bulk band structure and the symmetry- and layer-projected densities of states using a recently developed relativistic Green's-function formalism.¹¹ For the present calculations for Au on Pt(111) we made the following specific model assumptions. The real potential inside the muffin-tin spheres was taken for Pt as an earlier bulk potential^{1,9} and for Au from a superposition of atomic charge densities using the Hedin-Lundqvist exchange-correlation approximation. A uniform imaginary potential part is assumed as linearly increasing away from the Fermi energy.

The left panel of Fig. 2 shows spin-resolved photoemission spectra for Pt(111) and Au/Pt(111) at different

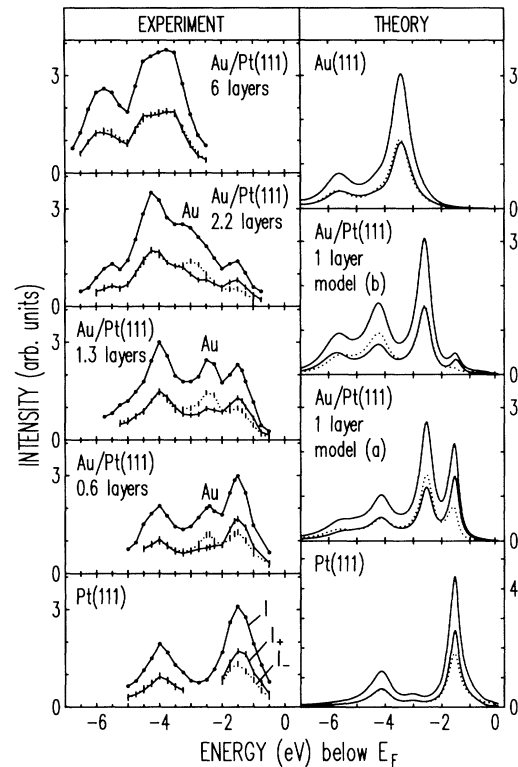


FIG. 2. Spin-resolved photoemission spectra obtained for normal incidence of linearly polarized radiation (21.2 eV) and normal electron emission. (Left panel) Experimental spectra for Pt(111) and different Au adsorbate coverages. The vertical dashes for I_+ and I_- are error bars. They represent the total error including the uncertainty of the light polarization and the detector asymmetry function. (Right panel) Calculated spectra for Pt(111) (bottom), Au(111) (top), and a monolayer Au adsorbate on Pt(111) for two different adsorption models: (a) in direct continuation of the Pt lattice; (b) coinciding with the second Pt layer, i.e., opposite stacking sequence.

coverages. The total photoemission intensity I is separated into the partial intensities I_+ (solid lower curve) and I_- (dotted curve) by means of the spin polarization P and the equation $I_{\pm} = \frac{1}{2} I (1 \pm P)$. I_+ and I_- denote then the electron intensities with spin direction parallel and antiparallel to the y axis.

The spectra in the lowest panel of Fig. 2 were measured for the clean Pt surface. Two photoemission peaks were obtained. In addition to the two Pt peaks at 1.5 and 4 eV, a peak at 2.5 eV below E_F (in the following called "Au peak"), which is obviously due to photoemission from the Au adsorbate, is found for the lowest coverage of 0.6 layer. Increasing the Au coverage further, one observes a strong decrease of the Pt peak at 1.5 eV below E_F until this peak is no longer found for a coverage of 6 layers. The intensity of the Au peak and two further peaks (they start to develop at a coverage of 1.3 and 2.2 layers at 4 and 5.7 eV below E_F , respectively)

increases with coverage. These peaks show only a slight shift to higher binding energy with Au coverage and converge to the two peaks in the 6-layer spectrum, which is very similar to that of a pure Au crystal.³

Partial intensities I_+ and I_- significantly different from each other (i.e., spin-polarized electrons) are only found for two of the peaks, namely, the Pt peak at 1.5 eV and the Au peak present up to a 2.2-layer Au coverage at 2.5 eV. No significant spin polarization is found for the 6-layer adsorbate. The ratio of I_+ and I_- for the Au peak is even larger than that determined for the Pt peak. Furthermore, I_- is larger in the Au peak whereas in the Pt peak I_+ dominates. This means that the spin-polarization reverses sign. The ratio of I_+ and I_- for the Pt peak is not reduced as a consequence of the gold adsorption. Even for 2.2 layers—a gold coverage at which the Pt substrate is certainly completely covered with gold—the electrons are strongly spin polarized. This result shows very clearly that the observed spin-polarization effect is not only a surface effect. It is more generally an interface phenomenon.

Different questions arise from these data. One is the question of why the spin-polarization effect is not observed for the 6-layer adsorbate, which should—as Pt(111)—also have a threefold symmetry. Another question regards the fact that the spin-polarization effect is already observed for a Au monolayer, a coverage at which the Au adsorbate itself has most probably only a sixfold symmetry. The Pt substrate seems thus to play an essential role in producing the spin-polarization effect from Au. Strong interactions between the Pt and Au levels are also suggested by the strong binding-energy shift of the Au level with Au coverage. The third point that should be discussed is the spin-polarization sign obtained for the gold peak which is opposite to that one of the platinum peak.

Answers to these questions are provided by photoemission calculations (right-hand panel of Fig. 2). For clean Pt(111), the spectra, and in particular the spin polarization of the peak near -1.6 eV, corroborate our earlier results.^{1,2} The theoretical spectra for a semi-infinite Au(111) crystal are in good agreement with the data measured for 6 layers. For a monolayer of Au on Pt(111), calculations were performed for the following two lateral placements of the Au lattice: (a) in direct continuation of the Pt lattice, and (b) coinciding with the second Pt layer, i.e., opposite stacking sequence. The total intensity spectra for these two cases exhibit, in addition to the clean Pt peaks, an Au-induced peak at 2.6 eV in good agreement with experiment. Comparing relative peak heights one has to bear in mind that the coverage in the experiment is not exactly one monolayer.¹² Consequently, the Pt features should be relatively stronger. Agreement in total intensities is then good for the normal stacking [case (a)], while for abnormal stacking the Pt peak near 1.5 eV is far too weak. For normal

stacking (a), the Au peak shows strong spin polarization with sign opposite to that of the Pt peak at 1.5 eV, in accordance with experiment. In contrast, abnormal stacking (b) leads to almost zero polarization for the Au peak and to a substantial polarization for the second Pt peak near 4.3 eV. Comparison with experiment thus clearly favors the normal stacking. In order to get further support for this conclusion Rutherford-backscattering measurements in combination with channeling were done to determine the Au adsorption site. These measurements are in very good agreement with normal stacking (a) and clearly not compatible with abnormal stacking (b).

The physical origin of the Au peak is elucidated by the symmetry- and layer-projected densities of states (DOS) shown in Fig. 3. At the energy of the Au photoemission peak at 2.5 eV below E_F there is a strong $\Lambda_{4,5}$ feature in the Au layer DOS and a smaller one in the first Pt layer DOS, located in a $\Lambda_{4,5}$ band gap of the Pt bulk. The initial state for the Au peak is thus identified as an adsorbate-induced surface state¹³ of $\Lambda_{4,5}$ double group symmetry. Although this state resides in the first two layers, the role of the remainder of the crystal for its formation is important. This is revealed explicitly by comparing the spin polarization of the Au peak for the two stacking sequences (Fig. 2). If the peak were exclusively due to the first two layers, its polarization should retain its magnitude and change sign upon reversal of the stacking order, since this reversal is equivalent to a π rotation of the

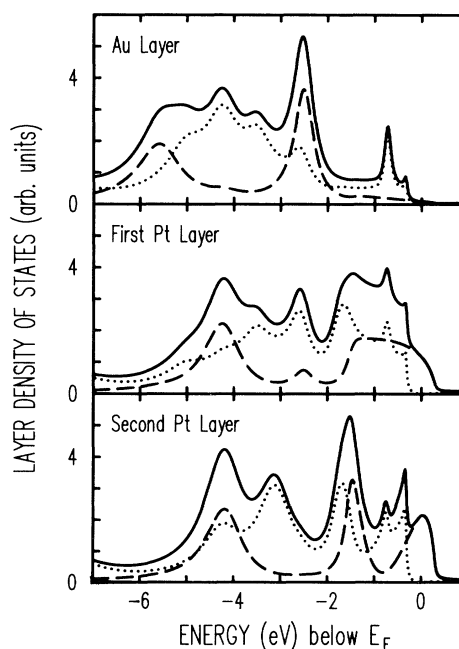


FIG. 3. Relativistic densities of states for the three topmost layers of a regular stacking of one monolayer of Au on Pt(111): symmetry types $\Lambda_{4,5}$ (---) and Λ_6 (····), and their sum (—).

first two layers (but not of the total system). Furthermore, we calculated the layer DOS for the abnormal stacking system and obtained practically identical results to those of the normal stacking. This maintains that the interference with the Pt substrate plays an important role in particular during the photoexcitation.

Summarizing, spin-resolved photoemission studies are performed with normally incident linearly polarized He I radiation and for normal electron emission from Pt(111) and Au layers on Pt(111). Strong spin polarization is observed for both electrons from Au and Pt. The spin-polarization effect for the Pt crystal is also observed for Au coverages up to 2.2 layers, i.e., the effect is not only a surface effect but more generally an interface phenomenon. The fact that the spin polarization from the Au adsorbate is obtained already for a Au monolayer coverage indicates that the Pt substrate plays an important role in the production of the effect. Calculations show that these photoelectrons correspond to transitions from a Au-induced surface state. The photoemission spectra are only compatible with a model in which the Au is adsorbed in sites which are a direct continuation of the Pt lattice. This model is confirmed by ion-scattering measurements. The present work clearly demonstrates the power of our recently discovered "linearly polarized light effect" for revealing surface properties.

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¹²The AST plot is compatible with layer growth but it does not explicitly prove it. To be sure that we have only a small number of atoms in the second layer, we have chosen 0.6 layer instead of 1.0 layer as representative for the monolayer regime. That the gold islands for the 0.6-layer coverage are large enough to represent the monolayer regime is strongly supported by LEED studies during Au monolayer growth, where we found no indication of a strong diffuse LEED pattern. We also did not see extra spots in LEED which means that the Au layers grow 1×1 .

¹³One might think of designating this state as "interface state," since [as in J. E. Houston, C. H. F. Peden, P. J. Feibelman and D. R. Hamann, Phys. Rev. Lett. **56**, 375 (1986)] a considerable amount of the wave function is located in both the Au surface layer and the first Pt layer. The designation "surface state" would also be appropriate, since the wave function is to a larger amount located in the Au layer than in the first Pt layer. We have chosen the designation "Au-induced surface state" on Pt(111) to point out the special role of the spin-polarization effect in revealing the contribution of the Pt surface to the Au electronic state.