Adsorbed rare-gas layers on Au(111): Shift of the Shockley surface state studied with ultraviolet photoelectron spectroscopy and scanning tunneling spectroscopy

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The energetic position of the Au(111) Shockley surface state is compared before and after adsorbing different rare gas monolayers (Ar, Kr, and Xe). We used ultraviolet photoelectron spectroscopy (UPS) and scanning tunneling spectroscopy (STS) in combination to get more complete information by using the advantages of both methods. For determining the energetic position and the effective mass of the surface state in UPS an analytic mathematical method is used, which takes the finite angular resolution of the analyzer into account. We performed STS scans for the pure Au(111) surface as well as covered with a monolayer Kr and Xe. For an accurate analysis it is possible to use an extended Kronig-Penney model to take into account the influence of the $23 \times \sqrt{3}$ reconstruction. We found that the first monolayer of a rare gas induces shifts of around 50–150 meV increasing with the gas atomic number, whereas a second monolayer has only a small influence of about 3–18 meV. Using an image potential model it is possible to characterize these shifts qualitatively. For a semiquantitative analysis the phase accumulation model is applied. Within this model we can describe the experimental data roughly with a Coulomb potential changing in dependence of the electron affinity and the dielectric constant of the rare gas.

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I. INTRODUCTION

Shockley surface states are two-dimensional systems which are formed by electron confinement due to the surface band gap of the bulk material and the vacuum barrier of the surface. They are of fundamental interest as model systems for a two-dimensional free electron gas. The properties energetic position $E_0$, effective mass $m^*$, and the lifetime were investigated thoroughly for different materials. Some discrepancies existed in earlier studies in particular for the comparison of ultraviolet photoelectron spectroscopy (UPS) and scanning tunneling spectroscopy (STS). New high-resolution experiments are in better agreement, cf., e.g., Refs. 1–4.

Due to its location at the sample surface the surface state can be influenced significantly by adsorbing various materials. Depending on the adsorbate the effect turns out qualitatively different. While some materials induce a shift, chemisorbed atoms and molecules often completely quench the surface state. Here we want to focus on the change of the properties $E_0$ and $m^*$ after adsorption of different rare-gas layers. These rare gases induce a shift towards higher energies, and the variation of the adsorbed gas offers a handle to investigate the underlying interactions in a systematic way. For the systems discussed here, the adsorbate layers can be described with simple models and they form incommensurate two-dimensional layers on Au(111), whereby the interaction with other substrates can be more complicated. In particular for the reconstructing Au(111) surface it is advantageous to use UPS and STS in combination. It helps to identify possible discrepancies between different experiments, e.g., due to variations in the sample preparation and allows a view on the results in a more complete frame.

With STS it is possible to measure the influence of adsorbates on the local density of states (LDOS) at different positions of the reconstruction. In order to determine the energetic position and the lifetime of the surface state we consider the local variation of the surface potential induced by the $23 \times \sqrt{3}$ reconstruction.

Angle resolved UPS allows to measure the energetic dispersion of the surface state for monolayers (ML) and multilayers of rare gases on Au(111). We include the finite angular resolution of the analyzer with an analytic model. With this we get more accurate data for the energetic position and the effective mass of the surface state.

For the discussion of the experimental results we use the surface potential and the so-called phase accumulation model, which allows us to classify these shifts with the properties electron affinity $E_A$ and the dielectric constant $\varepsilon$ of the rare gas. Using a surface potential, which was applied before for image states, we can classify the positions of the surface state qualitatively. It is also possible to explain the difference between an adsorbed rare gas monolayer and a multilayer of rare gas.

For more quantitative calculations we use the phase accumulation model which was applied before mainly for image states and quantum well states. Within this model it is possible to describe the barrier potential with either a step or a Coulomb potential. From the comparison of the measured and calculated positions of the surface state we find that the relevant potential for the surface state is essentially influenced by the electron affinity and the dielectric constant of the rare gas.

II. EXPERIMENT

The experiments were performed using low-temperature scanning tunneling microscopy (STM) which is combined with UPS in a common ultrahigh vacuum (UHV) system. It consists of two main chambers, a preparation chamber equipped with a high-resolution hemispherical electron en-
energy analyzer for UPS and an analysis chamber containing the low-temperature STM.

The STS data, either $dI/dV$ spectra measured with varying $V$ at a single position or $dI/dV$ maps measured for fixed $V$, were taken under open loop conditions by lock-in detection. The set point before switching off the feedback loop was between $V=-1$ V and $V=+1$ V and the tunneling current varied from $I=0.1$ nA to $I=0.3$ nA. For the single point spectroscopy data we used a modulation voltage of 7 mV$_{rms}$ and a frequency around 700 Hz. The lock-in time constant was set to 30 ms and the acquisition time was $\approx 80$ ms to avoid time constant effects. All STM and STS data were measured at $T$=5 K.

Our hemispherical analyzer has a radius of 125 mm. As a photon source we use HeI light with the energy of 21.2 eV. We have achieved with this setup a resolution of 10 meV. In the experiments presented here we chose slightly lower energy resolutions with higher counting rates. We used an angular acceptance of about $\pm 1^\circ$ and the data point distance is set to 5 meV. For the UPS measurement and the sample preparation the Au(111) samples were mounted on a manipulator, which can be cooled down below $T$=10 K, by means of a liquid helium flow cryostat. This manipulator allows transferring cold samples between the two chambers and into the STM. The angular accuracy of the manipulator is about $0.2^\circ$ for the adjustable rotation around the manipulator axis. The fixed angle perpendicular to the axis is $0^\circ \pm 0.3^\circ$.

The Au(111) single-crystal sample was prepared by repeated cycles of ion sputtering (1 keV Ar$^+$ or Kr$^+$ ions) and heating up to 900 K for 1 or 2 h. We checked the cleanliness of the sample by measuring the UPS peak of the Au(111) surface state, which is very sensitive to contamination. An ultimate check is imaging the sample in the STM. See for example Fig. 6, which shows the excellent sample quality after rare gas adsorption. Some contamination occurs during the low-temperature UPS measurements. We checked that the resulting decrease of the surface-state intensity was not significant on the time scale of the photoemission experiment. Alternatively also samples with a Au(111) film on mica were used. These films were produced in a separate vacuum chamber following the procedure of Ref. 23 by evaporation of a 100 nm Au film on freshly cleaved mica at $T$=360 °C. After introducing the Au/mica samples into the UHV system the surface was cleaned with ion sputtering (20 min) and heating (600 K). While the mesoscopic surface structure and the crystalline orientation was better defined for the Au(111) single crystal, the terrace areas were larger on the Au/Mica samples (cf. Sec. V).

A controlled number of rare-gas monolayers were dosed onto the samples by controlling the partial pressure with a quadrupole mass spectrometer and a leak valve. The exact time, partial pressure, and temperature for adsorbing well-defined monolayers of rare gases were determined with UPS by monitoring the $p$ signals of the corresponding rare gas. The energetic position of the measured $p$ signals gives us information about the film thickness of the adsorbed monolayer. The $n$th atomic layer has a signal which is shifted to lower energies compared to the first layer. We monitored the peak integral of a specific $p$ signal as a function of time to get the adsorption time and temperature at a given partial pressure. One example for this procedure is shown in Fig. 1. We used a constant rare-gas pressure (around 6 $\times 10^{-3}$ mbar) in the preparation chamber. Then we linearly decreased the temperature. When the signal of the $p$ peak emerges, the monitored monolayer begins to grow. At this point we held the temperature constant and stopped the time $\Delta t$ until the signal of the monolayer has saturated. This shows that the monolayer is complete. Because we fixed the temperature just below the limit for monolayer growth, the second monolayer cannot be adsorbed [cf. the phase diagram for Ar and Kr on Ag(111) (Ref. 28)]. If the temperature is set to a lower value (not shown) the signal decreases again after the first monolayer is complete. This is an indication that the second monolayer begins to grow and the signal of the first monolayer is attenuated. After the production of the desired coverage the gas flux is stopped which puts the pressure back into the UHV regime and the temperature is reduced far below the adsorption temperature. Both changes take only a few seconds and therefore stabilize the rare gas film in its final configuration for the UPS and STM/STS measurements.

This preparation method allows a perfect layer-by-layer growth which is shown in Fig. 2 for the adsorption of the first monolayer of Xe on Au(111). There the surface state peak of the clean Au(111) surface attenuates with increasing Xe coverage. Simultaneously a second peak appears at a higher energetic position. It corresponds to the shifted surface state on Xe/Au(111) and reaches maximum intensity at a coverage of one monolayer. STM images show that in the submonolayer regime the adsorbed Xe arranges in islands of several 1000 nm$^2$ [cf. also the STM images for Kr/Au(111) shown in Fig. 6]. Hence the energetic position does not shift continuously but the two systems Au(111) and Xe/Au(111) coexist in one sample.

### III. UPS Results

In the last decades angle resolved photoelectron spectroscopy has become an important tool for the observation of the
surface state of metals. For the correct interpretation of the experiments it is important to consider the finite energetic and angular resolution of the electron analyzer. This problem is described extensively in Refs. 29 and 30.

Here we give an analytical mathematical expression for the influence of the finite angular resolution on a photoelectron spectra of an electron state with parabolic dispersion. The energy dispersion of the surface state can be written as,

\[ E = E_0 + \hbar^2 k_x^2/2m^* \]  

(1)

with the onset of the parabolic surface state \( E_0 \), and its effective mass \( m^* \). The wave vector parallel to the surface is \( k_0 = \sqrt{2mE_{kin}/\hbar^2} \sin \theta \). \( E_{kin} \) is the kinetic energy of the photoelectrons after leaving the surface, \( m \) is the free electron mass, and \( \theta \) the angle of electron emission. In UPS only the parallel part of the \( k \) vector can be measured directly. The finite angular resolution of the electron analyzer applies not only for the angle \( \alpha \), which we are able to change by rotating the manipulator, but also for the angle \( \beta \) corresponding to the direction perpendicular to the manipulator axis, which is in our experiment adjusted at zero. We suppose that the distribution of the angles is Gaussian, because the aperture of the analyzer is small. A two-dimensional Gaussian function [Eq. (2)] gives the distribution around the adjusted angles \( \alpha_0 \) and \( \beta_0 \):

\[ P(\alpha, \beta) = \frac{1}{2\pi\sigma^2} \exp \left[ -\frac{(\alpha - \alpha_0)^2 + (\beta - \beta_0)^2}{2\sigma^2} \right]. \]  

(2)

In this formula \( \sigma \) is the angular resolution of the analyzer, which is assumed to be isotropic (\( \sigma = \sigma_{Gauss} \)).

For a realistic comparison between theory and experiment all angles have to be considered. The probability distribution of Eq. (2) can be transformed into an energetic one:

\[ P(\alpha, \beta) d\alpha d\beta = P(E) dE. \]

Because for the surface state both angles \( \alpha_0 \) and \( \beta_0 \) are small and \( \sigma_{Gauss} \ll 1 \), it is \( \theta^2 = \alpha^2 + \beta^2 \ll 1 \) and the energy (1) can be approximated as

\[ E = E_0 + c \theta^2 \text{ with } c = E_{kin}(m/m^*) \].  

(3)

The use of cylinder coordinates \( (\alpha = \theta \cos \varphi \text{ and } \beta = \theta \sin \varphi) \) gives

\[ P(\theta, \varphi) = \frac{1}{2\pi\sigma^2} \exp \left[ -\frac{(\cos \varphi - \alpha_0)^2 + (\sin \varphi - \beta_0)^2}{2\sigma^2} \right]. \]

(4)

Solving the integral in Eq. (4) leads to

\[ P(E) dE = d\theta \int_0^{2\pi} d\varphi P(\theta, \varphi) \]

\[ \times \int_0^{2\pi} d\varphi \left( \frac{2\theta \alpha_0 \cos \varphi + 2\theta \beta_0 \sin \varphi}{2\sigma^2} \right) \exp \left( \frac{\theta^2 + \alpha_0^2 + \beta_0^2}{2\sigma^2} \right). \]

(5)

The function (5) has to be convoluted numerically with a Lorentzian (finite lifetime). As only occupied states contribute to the spectra, the result is multiplied with a Fermi function corresponding to the sample temperature \( T \). Finally a convolution with a Gaussian is performed due to the finite energy resolution of the analyzer.

To fit the calculated set of spectra to the experiments we varied the following parameters: The energetic position \( E_0 \), the effective electron mass \( m^* \) of the surface state, the start angle \( \alpha_{start} \) from where the others follow in the same distance (here 1°), the angular resolution \( \sigma_\alpha \), the width of the Lorentzian \( \Gamma \), and the energy resolution \( \sigma_{Gauss} \).
To compare the measured data of the surface state to the calculated, we first have to subtract a background intensity. The background can be induced, for example, by satellites from the photon source or by signal from defects and it is approximated by a linear function. The structure of the background is angle independent for small angles. So we use the zero degree angle to fit a Fermi function multiplied with a linear function in a region without signal from the surface state. This is shown for one example in Fig. 3. With this fit we get the position of the Fermi energy $E_F$ very accurately as well, which is needed to calculate the absolute energetic position of the surface state.

Angle resolved UPS spectra for a monolayer and a bilayer krypton on Au(111) are presented in Fig. 4, spectra for other rare gases in Fig. 5. For each sample system just one set of parameters as described above is used to fit all spectra for different angles simultaneously. Only a constant factor is adjusted for each curve individually to match the peak amplitudes. Generally the agreement between the calculated curves and the experiment is very good.

For the krypton bilayer in Fig. 4(b) the signal on the lower energy shoulder is higher than the calculated curve. This could be caused by photon induced desorption of a part of the second monolayer induced by the helium lamp, which leads to a small signal of the first monolayer krypton. A similar effect is also visible for Ar/Au$_{111}$ [cf. Fig. 5(d)].

It has to be taken into account that the mean free path of the electrons is finite in the rare-gas layers. The surface state signal was around three to four times higher for the first monolayer krypton than for the second monolayer Kr. For this reason a higher accumulation time is needed for the second monolayer Kr.

The fit parameters $\sigma_r (0.7°–1.1°)$, $\sigma_{Gauss}$ (17 meV–45 meV), and $\Gamma$ (18 meV–40 meV) used in Figs. 4 and 5 are not independent. Partly they are influenced by measurement artifacts as, e.g., errors for the adjustment of the angles $\alpha_0$ and $\beta_0$ due to not perfectly flat sample surfaces, in particular for the Au/Mica samples. The angle $\beta_0$ was adjusted to 0° within ±0.3° at the sample holder. For the comparison with the experiment we also have to adjust the difference between the calculated starting angle $\alpha_{start}$ and zero which could be ±0.5°. The parameters $E_0$ and $m^*$ for the different samples will be summarized in Sec. V.

With the fitting routine we were much more sensitive for calculating the energetic position and the effective electron mass for the dispersion relation of the surface state than by simply measuring peak positions. For example, the lowest peak position in Fig. 4(a) would indicate $E_0 = -347$ meV which is 27 meV too high, mainly because of the systematic error induced by the asymmetric broadening due to the finite angular resolution.

IV. STS RESULTS

With STS we are able to measure the energetic position of the surface state onset very accurately. It is possible to change the position of the tip and measure in different regions of the reconstruction and far away from step edges and defects.

The periodic Au(111) reconstruction ($a=6.3$ nm) can be separated into a fcc, a hcp, and two transition regions. Figure 6 shows two STM images, one overview picture which shows the clean Au(111) surface and parts covered...
with 1 ML krypton [Fig. 6(a)], and an atomically resolved image of the Au(111) reconstruction with one monolayer krypton adsorbed [Fig. 6(b)]. The few bright dots on the uncovered Au(111) terraces in Fig. 6(a) correspond to small Kr islands located at the step edges but partly also at the knees of the herringbone reconstruction. White horizontal lines indicate that some of these islands are shifted by the tip. The dark spots on the rare gas covered part are vacancies in the Kr film. Some of them occur as horizontal lines also indicating a tip surface interaction. The 23 × 3 reconstruction is visible on both, the clean and the Kr covered, areas. The bright dots in Fig. 6(b) represent the atomic structure of the krypton layer, which is incommensurate to the Au(111) surface. The two bright stripes are the transition regions and the part inside is the hcp region. Outside the transition region, the fcc region is imaged as the broader part.

The influence of the reconstruction on the surface state was considered in Ref. 15 by applying a Kronig-Penney model for the periodic effective potential with the width $a_1$ in the fcc regions and $a_2$ in the hcp regions:

$$V_{KP}(x) = \begin{cases} V_1 & \text{for } 0 \leq x < a_1 \\ V_2 & \text{for } a_1 \leq x < a_1 + a_2 \end{cases}, \quad V_{KP}(x + a_1 + a_2) = V_{KP}(x).$$

A special lock-in technique for mapping the surface potential spatially resolved was used in Ref. 16. A strongly structured potential was found at the transition regions of the reconstruction in addition to the difference between hcp and fcc sites. We obtained a similar result by observing that the Kronig-Penney potential as used in Ref. 15 could not reproduce all features in the experimental STS spectra. The agreement was significantly better if we extended the Kronig-Penney model with δ distributions at the narrow transition regions. The extended Kronig-Penney potential $V_{EKP}(x)$ can be summarized as

$$V_{EKP}(x) = V_{KP}(x) + V_\delta(x) \text{ with } V_\delta(x) = A[\delta(x) + \delta(x - a_1)].$$
The intensity $A$ of the $\delta$ distribution can be either negative or positive. The potential also satisfies the periodicity condition:

$$V_{\text{EKP}}(x + a_1 + a_2) = V_{\text{EKP}}(x).$$

Here we compare the measured STS data with the calculated density of states of the extended Kronig-Penney model. The two-dimensional local density of states LDOS ($E,x,y$) can be written as

$$\text{LDOS}(E,x,y) = \frac{V}{2\pi} \int_{\epsilon(k_x,k_y)}^{dE} |\psi_{k_x,k_y}(x,y)|^2 dk_x dk_y,$$

where $\epsilon(k_x,k_y)$ is the electron dispersion relation. To consider the one-dimensional influence of the reconstruction we have to split the wave function in a free-electron like $y$ component and a Bloch component in $x$ direction:

$$\psi_{k_x,k_y}(x) \propto e^{ik_yy} u_{k_x}(x).$$

Here $u_{k_x}(x)$ is a function with the periodicity of the reconstruction. From this we get for the LDOS ($E,x$),

$$\text{LDOS}(E,x) \propto \int_{\epsilon(k_x) \leq E} |\psi_{k_x,k_y}(x,y)|^2 \frac{dk_x}{\sqrt{E - \epsilon(k_x)}}.$$  

With the potential $V(x)$ we have the complete Hamiltonian and we are able to calculate the wave function within the transfer matrix formalism. The density of states is evaluated numerically. The calculation can be compared with the STS spectra after a convolution with a Gaussian and a Lorentzian function.

For Au(111) and Xe/Au(111), respectively, measured raw data are shown in Fig. 7. The measured STS spectra show the step-shaped onset of the surface state at $V \approx -0.5$ V and $V \approx -0.35$ V, respectively, superimposed on a background which is given by the transmission coefficient. Using

FIG. 6. (a) Top: STM image ($150 \times 150$ nm$^2$) of Au(111) on mica partly covered with Kr; bottom: line profile marked in the top image (b) STM image ($7 \times 7$ nm$^2$) of one stripe of the reconstruction of Au(111) on mica covered with a monolayer krypton (sample voltage $-0.93$ V, tunneling current 0.24 nA).

FIG. 7. Measured $dI/dV$ spectra for a clean Au(111) surface (solid) and a Xe covered Au(111) surface (dashed). Each spectrum is an average of 25 single spectra which enhances the signal/noise ratio. For both systems the spectra were taken in the center of the hcp region as well as in the fcc region.
with the tip surface distance \( d \) and the mean work function \( \overline{\phi} \), the background signal can be fitted to the low-voltage tail of the spectra, assuming a constant bulk density of states. In addition one observes peaks and kinks which display characteristic differences for measurements in the hcp and fcc region.

For the calculated data we adjusted four free parameters: \( a_1, \Delta V=V_1-V_2, \) and \( A \), which determine the shape of the spectra, and the absolute energetic position \( V_i \). We used an effective electron mass of \( m^*=0.24m_e \), which is the average value measured for the Au(111) surface state with UPS (see Sec. V). A possible change of \( m^* \) by the rare gas is negligible for this calculation (cf. Table I). For a clean surface the lifetime of the Au(111) surface state is between \( \tau=31 \text{ fs} \) (Ref. 3) and \( \tau=35 \text{ fs} \). For the system Xe/Ag(111) a lifetime decrease of the surface state was observed.\(^9\) For Au(111) we could neglect this effect and use the same Lorentzian line width of 18 meV for all coverages. This indicates that the lifetime change is not strong compared to the lifetime of the clean surface. The width of the Gaussian is \( \sigma=5 \text{ meV} \), which is the energy resolution of our experimental setup.\(^39\) We notice here that the observed agreement in the width of the step onset and the first peak in the hcp region (cf. Fig. 8) corroborates the lifetimes of Refs. 2 and 3. The sum \( \sigma=a_1+a_2=6.3 \text{ nm} \) is the period length of the reconstruction.\(^33\) From different STM pictures no significant change of the reconstruction was found after adsorbing different rare gases, in contrast to the significant change of reconstruction after adsorbing oxygen.\(^40\)

Table I. Energetic position of the surface state for different rare-gas systems on Au(111) measured with STS and UPS. The effective electron mass was determined from the UPS fit described above. For 2 ML Xe/Au(111) only the normal emission spectrum was taken. For some systems we show values for different samples. Some complement values for Cu(111) and Ag(111) are given in Ref. 7–9.

<table>
<thead>
<tr>
<th>System</th>
<th>Energetic position UPS (meV)</th>
<th>Energetic position STS (meV)</th>
<th>Effective mass ( m^*/m_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(111) single crystal</td>
<td>(-429 (T=300 \text{ K})) and (-487 T=30 \text{ K}) from Ref. 49</td>
<td>(-499 \text{ to } -494)</td>
<td>0.26 and 0.255 from Ref. 49</td>
</tr>
<tr>
<td>1 ML Xe/Au(111) single crystal</td>
<td>(\ldots)</td>
<td>(-349 \text{ and } -363)</td>
<td>(\ldots)</td>
</tr>
<tr>
<td>Au(111) Mica</td>
<td>(-442 \text{ and } -453)</td>
<td>(-465 \text{ and } -469)</td>
<td>0.245 and 0.23</td>
</tr>
<tr>
<td>1 ML Ar/Au(111) Mica</td>
<td>(-400)</td>
<td>(\ldots)</td>
<td>0.24</td>
</tr>
<tr>
<td>1 ML Kr/Au(111) Mica</td>
<td>(-374)</td>
<td>(-414)</td>
<td>0.27</td>
</tr>
<tr>
<td>2 ML Kr/Au(111) Mica</td>
<td>(-356)</td>
<td>(\ldots)</td>
<td>0.28</td>
</tr>
<tr>
<td>1 ML Xe/Au(111) Mica</td>
<td>(-315)</td>
<td>(-319)</td>
<td>0.25</td>
</tr>
<tr>
<td>2 ML Xe/Au(111) Mica</td>
<td>(-312)</td>
<td>(\ldots)</td>
<td>(\ldots)</td>
</tr>
</tbody>
</table>

\[
T(d,V) \propto \exp \left\{ -2d \sqrt{\frac{2m_e}{\hbar^2} \left( \frac{\overline{\phi} - eV}{2} \right)^2} \right\}
\]

Figure 8 shows STS data for a single Au(111) crystal and Kr on Au(111) on mica after subtraction of the background signals as discussed in the context of Fig. 7. The experimental spectra are compared with the calculated LDOS. The overall shape of this spectrum roughly corresponds to the step function expected for the two-dimensional density of states. In the hcp region of the reconstruction we see in addition a peak at the step onset, which is caused by the one-dimensional influence of the reconstruction. In the fcc region the surface state onset exhibits a reduced LDOS. The essential structures are reproduced by the model, i.e., the first peak in the hcp region at the surface state onset, as well as the feature at the second band gap of \( E(k_z) \) at \( V=-350 \text{ mV} \) for clean Au(111), respectively, \( V=-270 \text{ mV} \) for Kr/Au(111). The main parameter for the amplitude of the peak in the hcp region is \( \Delta V \) and it changes from 18–39 meV for pure Au(111), to 50 meV for Kr/Au(111), and from 65–70 meV for Xe/Au(111). This indicates that also the local modulation of the potential is modified by the rare-gas layer.

Without adding the \( \delta \) distributions to the Kronig-Penney model, we could only find agreement between calculated and measured LDOS with extremely asymmetric ratios \( a_1/a_2 \), in particular concerning the feature at the second band gap. This would be contradictory to experimental measured reconstruction widths.\(^41,33\)

Here we focus on the spatially averaged potential which can be calculated as
FIG. 8. STS spectrum of the surface state (a) of a clean single crystal and the (b) for Kr/Au(111) on mica, in the hcp (left) and the fcc (right) region, respectively. The calculated LDOS curves are plotted with dashed lines and the experimental $dI/dV$ spectra are normalized to the calculated curves. We used $a_1=3.15$ nm, $\Delta V=18$ meV, $\langle V \rangle = -494$ meV, and $A=-22$ meV nm for Au(111) and $a_1=3.15$ nm, $\Delta V=50$ meV, $\langle V \rangle = -414$ meV, and $A=+35$ meV nm for Kr/Au(111), respectively. Because the different fit parameters have independent effects on the calculated LDOS, it is possible to arrive at unique parameter sets by manually fitting the experimental curves.

$$\langle V \rangle = \frac{a_1 V_1 + a_2 V_2 + 2A}{a_1 + a_2}.$$  

Hence by considering the extended Kronig-Penney model we are able to calculate the energetic position of the surface state more accurately. The value of $\langle V \rangle$ which is given by the STS measurement far away from step edges and defects can be compared to the energetic positions observed with UPS, which averages over a macroscopic area.

V. DISCUSSION

One influence for the energetic shift of the surface state induced by the rare gas, may be the change of the work function. We determined the work function for, e.g., clean Au(111) to 5.36 eV and Xe/Au(111) to 5.04 eV by using the full energy width of the UPS spectrum, i.e., the difference between the Fermi energy $E_F$ and the low energy onset of the secondary electrons $E_{SE}$, as $\phi=h\nu-(E_F-E_{SE})$. For these work function spectra a sample bias of $-5$ V was applied. Considering only the work function change a small shift of the surface state to lower energies would be expected but we get an upward shift of the surface state after rare-gas adsorption, in opposite direction to the work function change. So other effects have to be considered.

UPS averages over a macroscopic area of the sample (in our measurements an area of about 3 mm diameter), and therefore includes defect induced signals. The data from STS are measured on large plane areas of the surface. So by combining both methods we can estimate the possible influences from step edges and other defects, which induce a shift to higher energies, an asymmetry of the surface state peak in UPS (Ref. 44), and local variations in the density of states. 45, 46

In Table I the measured energetic positions of the surface state for different rare-gas systems are given. The comparison between the measured UPS and STS data shows the effect of spatial averaging in UPS. The energetic position of the surface state is always lower in STS, which is consistent with the arguments before. In addition the influence of the tip-surface potential47 shifts the surface state as measured with STS about 15 meV to lower energies for the clean Au(111) surface. 48

The surface state also shifts by using different types of Au(111) samples. With the STM we observed a larger number of small terraces for the single crystal used here than for Au(111) on mica. We think that this was caused by some residual stress of the crystal in the sample holder, because we observed distorted shapes for the herringbone reconstruction. On the other hand, there are cloughs between the different Au crystallites on mica. Inside these cloughs no surface state exists. The small single crystallites for Au(111) on mica may be mechanically stressed too. Stress affects the shape of the reconstruction 35 and causes a shift of the surface state. 50 From four series of data we get the position of the surface state of the Au(111) single crystal between $-494$ meV and $-499$ meV in STS. On Au(111) on mica we have measured a position of the surface state around 30 meV higher: between $-465$ meV and $-469$ meV (see Table I).

In addition it has to be noticed that the Au(111) on mica sample is not as plane as the single crystal. So the angular distribution can be broader in UPS.

For an exact comparison we have to consider the different temperatures of the measurements. 51 Higher temperatures induce a shift of the surface state of about 0.2 meV/K to higher energies. This is most important for the UPS data of the Au(111) single crystal [Fig. 5(b)], which were measured at room temperature. For the comparison of the STS and the UPS data at temperatures from 5 K to 50 K this effect is small because it is induced by a changing of the lattice parameters which levels off at low temperatures. We observed no significant change of the effective electron mass $m^*$ (cf. Table I) after adsorption of different rare gas monolayers, in agreement with results for rare gases on Ag(111) and Cu(111). 7-9

Now we summarize and discuss the data for the several different rare-gas systems measured in this work. In the UPS data of Table I and Fig. 9 we can see that the shift of the surface state is small after adsorbing a second monolayer, whereas different rare gases induce significantly different shifts. The corresponding STS data for the clean and 1 ML systems are systematically shifted to lower energies due to the local character of the measurement 44-46 and the influence of the tip-surface potential 47,48 as discussed above. But the
In the vacuum the potential is given by

\[
V_a = -\frac{e^2}{8\pi\varepsilon_0(\varepsilon + 1)z} \cdot \frac{e^2(\varepsilon - 1)}{16\pi\varepsilon_0(\varepsilon + 1)(t-z)} + \frac{e^2(\varepsilon - 1)(t+2z)}{16\pi\varepsilon_0(\varepsilon + 1)(t+z)} + \delta V_i(z) - \varepsilon \delta V_i(z) - \varepsilon
\]

with

\[
\delta V_i(z) = -\frac{e^2}{2\pi\varepsilon_0(\varepsilon + 1)} \cdot \sum_{k=2}^{\infty} \frac{(-1)^{k-1}}{k^2} \cdot \frac{1}{(\varepsilon + 1)^k}.
\]

Here \(\varepsilon_0\) is the vacuum dielectric constant, \(\varepsilon\) the dielectric constant of the rare gas film, \(t\) the thickness of the film, \(e\) the elementary charge, and \(\varepsilon\) the electron affinity of the rare gas (see below for \(\varepsilon\) values used). To overcome the singularity at \(z=t\) the potential is interpolated linearly within a layer of 0.3 nm thickness.\(^{17,18}\)

For \(\varepsilon\) we have used the bulk values given in the Refs. 52 and 53: \(\varepsilon_{Ar}=1.56\), \(\varepsilon_{Kr}=1.78\), and \(\varepsilon_{Xe}=1.98\). Low-energy electron diffraction studies of rare gases on metals have shown that the lattice parameter of the first rare-gas monolayer can be different compared to the bulk.\(^{54}\) This small influence is neglected in the following calculations.

Using this potential, we now qualitatively interpret the shifts induced by different rare gases and coverages. For a quantum well of the same width but with a higher barrier the electronic states shift to higher energies. If the width is getting narrower the states also shift but the relative effect is much stronger. In Fig. 10(a) we calculate the potential for different layer thicknesses of Xe. One can see that inside the quantum well, for energies around or below the Fermi energy \(E_F\) the width is the same for all rare-gas film thicknesses. Additional layers of Xe change the quantum well mainly at the top. So the influence on the surface state, with an energetic position some hundred meV below the Fermi energy, is small. If the rare gas is changed we get a small change at the top of the potential but the width changes at the bottom [Figs. 10(b) and 10(c)]. So we see that from Ar to Xe the potential is getting narrower and we can explain the large shift induced by using different rare gases, compared to the small shift of additional rare-gas monolayers.

In Fig. 10(c) it is visible that the width of the potential changes the most between the clean Au(111) surface and the different rare gases. This is in disagreement with the experiment, for which the relative shifts are of similar size going from the clean surface to Ar, Kr, and Xe. Possible reasons for this disagreement will be discussed later.

Quantitative values for the energetic positions of the surface state can be calculated using the phase accumulation model. The model consists of two reflection phases: the barrier phase and the crystal phase. If the sum of the barrier phase \(\Phi_B\) and the crystal phase \(\Phi_C\) is a multiple of \(2\pi\), i.e., \(\Phi_B + \Phi_C = 2\pi n\), bound states (so-called image states) occur. For the special case of the surface state the sum \(\Phi_B + \Phi_C\) must be zero.

This model is well suited to describe the position of the image states and the quantitative results are sensitively dependent on the exact position of the image plane \(z_0\).\(^{19,20,55}\)

The image state properties of different metal adsorbate interfaces were studied in the past (see e.g., Refs. 17, 18, 56, and 57). The model is described in detail in Refs. 19, 20, 57, and 58.

The crystal phase can be calculated as in Refs. 21 and 55 by

\[
\delta V_n(z) = -\frac{e^2}{4\pi\varepsilon_0(\varepsilon + 1)^2} \cdot \sum_{k=1}^{\infty} \frac{(-1)^k}{k^2} \cdot \frac{1}{(\varepsilon + 1)^k}.
\]
In this equation $E_L = -1.05$ eV and $E_U = 3.35$ eV are the positions of the lower and upper surface band gap of an Au(111) single crystal.\(^1\)

The experimental results in Table I and Fig. 9 show that the influence of the second rare gas monolayer is small. Therefore it is useful to compare the energetic position of the surface state calculated for an infinite number of monolayers with the measured data of one and two monolayers rare gas.

Two possible potential models for the barrier phase are the step potential and the Coulomb potential. Both are interesting to consider because they, respectively, take into account different aspects of the rare-gas layer and the substrate.

The image potential of Eq. (6) changes for an infinite thickness of rare gas to a Coulomb potential considering the dielectric constant $\varepsilon$ of the rare gas:

$$V = -\frac{e^2}{4\pi\varepsilon_0\varepsilon_4 z^2}. \quad (7)$$

For a clean metal surface $\varepsilon = 1$ the barrier phase for the Coulomb potential as given in Ref. 19 can be rationalized using the binding energies of the image states ($n = 1, 2, 3, \ldots$) with respect to the vacuum energy $E_V$ in the limit of an infinite barrier at the crystal surface ($\Phi_c = -\pi$) (Ref. 20):

$$E_n - E_V = -\frac{1}{16}E_{Ryd} \frac{1}{n^2}. \quad (Ref. 58)$$

This gives for $\varepsilon = 1$ (cf. Ref. 58)

$$\Phi_{B,Coul}(E) = \sqrt{\frac{E_{Ryd}/4}{E_V - E - E_F}} - \pi.$$

A dielectric constant $\varepsilon \neq 1$ changes the Rydberg energy

$$E_{Ryd}(\varepsilon) = \frac{m_e e^4}{32\pi^2\hbar^2(\varepsilon\varepsilon_0)^2} = \frac{13.6 \text{ eV}}{\varepsilon^2}. \quad (Ref. 20)$$

Together with the shift of the vacuum energy by the electron affinity $E_A$ of the rare gas this results in

$$\Phi_{B,Coul}(E, \varepsilon) = \sqrt{\frac{3.4 \text{ eV}/\varepsilon^2}{E_V - E_A - E}} - \pi.$$
reason for this choice will be discussed below.

First we discuss the energetic positions calculated with a step potential in Fig. 11. In Fig. 11(b) it is visible that the calculated shifts disagree qualitatively with the experiment in case of Kr and Xe though the magnitude of the rare-gas induced shifts is of the order of 0.1 eV as in the experiment. The only influence considered here is the electron affinity EA of the rare gas. Its sign determines the main direction of the shift.

In Fig. 12(b) the calculated relative shifts for the different adsorbed rare gases using the Coulomb potential occur in the same qualitative direction as experimentally observed. The graph shows the experimental UPS values compared to the calculated ones for the step potential. For Kr and Xe both experimental values, for 1 ML and 2 ML, are given.

To summarize the discussion, we started from the experimental observation that the main shift of the surface state

FIG. 11. (a) The crystal phase (fat dashed) and the barrier phase (thin dashed) and their sum (solid) are plotted for pure Au(111) and Ar, Kr, and Xe on Au(111) for a step barrier. The vertical and horizontal thin lines show the adjustment of the phase offset \( k_{\perp} z_0 \) for Ar/Au(111). In the inset the region determining the energetic position is magnified. (b) Energetic position of the surface state of clean Au(111) and after adsorbing different rare gases. The graph shows the experimental UPS values compared to the calculated ones for the step potential. For Kr and Xe both experimental values, for 1 ML and 2 ML, are given.

FIG. 12. (a) The crystal phase (fat dashed) and the barrier phase (thin dashed) and their sum (solid) are plotted for pure Au(111) and Ar, Kr, and Xe on Au(111) for a Coulomb potential. The vertical and horizontal thin lines show the adjustment of the phase offset \( k_{\perp} z_0 \) for Ar/Au(111). (b) Energetic position of the surface state of clean Au(111) and after adsorbing different rare gases. The graph shows the experimental UPS values compared to the calculated ones for the Coulomb potential. For Kr and Xe both experimental values, for 1 ML and 2 ML, are given.

For a quantitative comparison of calculation and experiment the exact values of \( \epsilon \) for the different rare gases would be essential. However, a correction of the bulk parameters was needed, e.g., to explain the experimental results for studies of the image states. For thin rare-gas films this may be connected to a lattice constant different to the bulk value. To summarize the discussion, we started from the experimental observation that the main shift of the surface state...
energy is already induced by the first ML of rare gas and we compared calculations for a half space of rare gas above the sample surface within the phase accumulation model using a step and a Coulomb potential. In this way we were able to distinguish between the general trends given by the macroscopic parameters $E_A$ and $\epsilon$ of the different rare gases. It is interesting to compare this to the interpretation of the surface state shift as due to the Pauli repulsion between the rare-gas atom and the metal, which for which also the interaction with the rare-gas atoms directly at the surface is crucial.

For a better determination of the surface state position a calculation is needed, which takes into account the potential near the surface on an atomic scale, as used for the surface- and image-state properties of clean Au(111) and Ag(111). Of course these results have to be combined with the influence of the rare gas, as it was done for the case of image states for Ar/Cu(100). But the main effects will be described already with semiquantitative model potentials as used here.

VI. CONCLUSION

On a Au(111) surface with a controlled number of adsorbed rare-gas monolayers we characterized the surface state with STS and UPS. The combination of both techniques helped to identify possible influences of, e.g., step edges and other defects and it presents a rather complete view of the effects induced by the rare-gas coverage.

For the angle resolved UPS data we included the finite angular resolution in a model which can be calculated analytically. For the STS data an extended Kronig-Penney model reproduced the structures induced by the influence of the $23 \times \sqrt{3}$ reconstruction and helped us to quantify the surface-state onset. Calculating $\langle V \rangle$ from this model we can evaluate the spatially averaged energetic position of the surface state. The rare gas on Au(111) induces a shift of the surface state. We measured that the first monolayer of the different rare gases produces a shift between 50 to 150 meV and the second monolayer adds only a small additional shift of around 10 meV.

These shifts are interpreted qualitatively by an image potential, which was used for image and quantum well states before. Assuming that the dielectric constant and the electron affinity are the main characteristic parameters of the rare gas for the shift of the surface state, we can calculate the position of the surface state with a phase accumulation model. This model is applied to a rare-gas film of infinite thickness, because already the influence of the second monolayer was found to be small in the experiment. For the barrier phase we used different potentials. The step potential only includes the electron affinity of the rare gas, whereas the Coulomb potential additionally comprises the dielectric constant $\epsilon$. The comparison with the measured surface-state positions reveals that a realistic phase has to take into account both, the dielectric constant and the electron affinity. However, for a quantitative theoretical determination of the rare-gas influence on the surface state the electronic interactions will have to be considered on an atomic scale using more advanced and therefore more complex techniques.

Note added in proof. It is interesting to compare the bandgap features in the STS spectra (cf. Fig. 8) with the density of states of the surface-state electrons on the reconstructed Au(111) surface as determined in Ref. 63 using angle-resolved photoemission.

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