Review

Morphology and electronic structure of gold clusters on graphite: Scanning-tunneling techniques and photoemission

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Abstract

We present an experimental study for the geometric and electronic properties of gold clusters grown in nanometer sized pits on graphite in a broad size range from a few ten to more than $10^4$ atoms per cluster. The growth process and the morphology were characterized in detail with scanning tunneling microscopy, transmission electron microscopy and ultraviolet photoelectron spectroscopy (UPS). The size-dependent quantized electronic structure detected with scanning tunneling spectroscopy (STS) for small gold clusters with a few ten up to about $10^4$ atoms per cluster is discussed qualitatively in terms of simple models. For the specific case of the confined Shockley surface state on the top (111) facets of large gold clusters with more than $10^4$ atoms per cluster we were able to detect the quantized electronic structure with both techniques, STS and UPS. The analysis shows a quantitative agreement between the density of states extracted from the STS spectra by averaging over the cluster size-distribution, and UPS after a deconvolution of the dynamic final state effect, which leads to a systematic asymmetric broadening of all spectral features. These results for the model system of gold clusters on graphite highlight general features of the cluster–surface system and they demonstrate the consistent combination of STS and UPS for the study of clusters on surfaces.

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1. Introduction

Spectroscopy of the electronic properties of clusters on surfaces is still ‘work in progress’: although quite an amount of data has already been collected, the understanding of the observed effects is much more preliminary than in the case of free clusters. Partly this is due to the increase in complexity which follows from the cluster–surface interaction disturbing the symmetry and isotropic surroundings of the free clusters in vacuum. But there are also experimental reasons. Experiments for the controlled deposition of mass selected clusters without any fragmentation or coalescence are not yet a standard experiment. Even if one is able to deposit mass selected clusters on a surface, small clusters may have different isomers and orientations on the surface, and spatially averaged spectra such as obtained by photoelectron spectroscopy or related techniques may not show the full information included in the electronic structure of the single clusters.

An alternative approach is the study of individual clusters using scanning probe techniques, in particular scanning tunneling microscopy and spectroscopy. We followed this route using metal clusters grown on graphite surfaces at preformed nanometer sized pits acting as well defined nucleation centers. Scanning tunneling microscopy (STM) was used
to characterize the size-dependent cluster morphology. This is an important prerequisite for understanding the electronic cluster-properties, which could be measured for individual clusters using low-temperature scanning tunneling spectroscopy (STS). Because the interpretation of scanning tunneling spectroscopy on individual clusters is complicated and still a topic of current research, we used ultraviolet photoelectron spectroscopy (UPS) as a complementary method. It gives momentum-resolved information on the occupied electronic states and the cluster–surface interaction. In addition it helps us to study the cluster growth process.

For free clusters in vacuum alkali metal clusters were used in a large number of experiments as a kind of model system, because their electronic properties can be described very well with the model of an idealized free electron metal [1]. In the case of clusters at surfaces less reactive metals are preferred. Clusters in a free beam in vacuum are measured within a few ms after their production, therefore reactivity is less critical than for clusters on a surface, for which ultrahigh vacuum conditions are required to keep the sample clean for at least some hours. Close to the Fermi level silver is a nearly free electron metal where the electron delocalization leads to strongly cluster-size dependent states. However, the influence of the d-electrons is not negligible, e.g., for the optical properties of the clusters. This interesting electronic structure is combined with a moderate chemical reactivity, which may be the reason why silver is used in many of the experiments for clusters on surfaces [2–4]. From the practical point of view gold is an even more suited material for the experiments on clusters at surfaces because its low chemical reactivity ensures reproducibility and long measuring periods with hardly any contaminations. However, the theoretical quantum-mechanical treatment of gold often proves to be a challenge. The large atomic number leads to pronounced relativistic effects with consequences on various properties, as e.g., bond lengths, catalysis, ionization potentials, magnetic properties, and many more. On the other hand Au clusters at surfaces exhibit remarkable and unexpected behavior, the most prominent being the chemical activity in catalytic processes. A fair amount of experimental evidence for the role of supported Au clusters in catalysis has been presented [5,6]. The detailed mechanisms and the connection to the electronic structure are the topic of ongoing investigations [7]. Spectroscopic data, as obtained by scanning tunneling spectroscopy and photoelectron spectroscopy is expected to play a key role in this area of research.

For the case of gold clusters on graphite we have investigated a broad range of cluster sizes, from a few ten up to more than 10⁴ atoms per cluster. For small clusters without facets scanning tunneling spectroscopy data measured for a large number of clusters show remarkably systematic features changing with the cluster size. But a quantitative interpretation might require not only a detailed analysis of the electron confinement in three dimensions but also an inclusion of special transport phenomena in the tip–cluster–surface system. The tunneling spectroscopy data for large clusters are dominated by a confined Shockley surface state, which can be described quantitatively considering the confinement to the hexagonal (111) facets on top of the clusters.

Using STM to measure the well defined faceted cluster shape of these larger clusters, and including the cluster surface interaction for the interpretation of final state effects in the photoemission process, we arrived at a quantitative agreement between the STS data on individual clusters and the UPS spectra which average over a large number of clusters.
2. Experimental methods

The main experimental techniques used within this work for the study of the geometric and electronic structure of gold clusters at surfaces are scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and ultraviolet photoelectron spectroscopy (UPS). Each method requires a sophisticated analysis to account for the respective specific effects. In this section a short qualitative overview is given and the reader is referred to the literature for a more detailed and quantitative discussion. Some particular aspects concerning experiments with supported clusters are mentioned, which will become important for the discussion in the subsequent sections.

Scanning tunneling microscopy is a powerful method for topographic imaging in real-space. Developed in 1982 [8,9] it has become an important tool for the surface analysis of metals or semiconductors down to atomic resolution. An atomically sharp tip is brought in close vicinity to the sample surface and a bias voltage in the range of mV to V is applied. The resulting tunneling current, typically of the order of 1 nA, is exponentially dependent on the tip–sample distance and can thus be used to determine the topography. In the measurements presented in this work we used the constant current mode where the tunneling current serves as a control variable for a feedback loop which adjusts the tip–sample distance according to the user defined set-point current. The surface morphology is obtained by scanning the surface line-by-line in the lateral direction. Typical resolutions are about 100 pm in the lateral direction and 1 pm vertically. A more detailed description of STM can be found in Ref. [10].

The STM images do not represent the surface geometry directly. For low voltages they correspond to surfaces of constant density of states (DOS) at the Fermi level $E_F$ [11,12]. In particular for the investigation of three-dimensional morphologies, such as supported clusters, the tip geometry has an important effect on the STM image. Whereas the height is determined correctly if a constant density of states is assumed, the lateral diameter is strongly overestimated (see Fig. 1). Nevertheless, in the case of flat facets on top of the clusters the facet shapes and areas can be obtained accurately from the STM measurements. On the substrate but also on the flat facet the tunneling current is focused on a small protrusion (marked as a small triangle at the leftmost tip profile in Fig. 1) on the

![Fig. 1. Schematic representation of the tip movement across a cluster (bottom). The resulting line profile is shown at the top. It directly provides information about the cluster height $h$ and the facet diameter $d_{\text{facet}}$, whereas the base diameter is strongly increased by the tip.](image)
The tip–sample interaction and non-ideal feedback characteristics lead to lateral forces which can be large enough to displace metal clusters on a graphite surface [14]. In order to reduce these forces low tunneling currents of about $I = 10, \ldots, 100\,\text{pA}$ and gap voltages in the range of $V \approx 2\,\text{V}$ were used within this work. These settings increase the tip–surface distance and reduce the probability of tip induced cluster displacement. However, the large voltage allows contributions to the tunneling current from states considerably far above or below the Fermi level (dependent on the polarity). Furthermore, if the tip–surface distance [15] is not small compared to the cluster diameter, simple geometric arguments predict additional possible tunneling paths directly into the substrate when the tip is positioned above the cluster. As a consequence the measured height may deviate from the actual morphology. In Fig. 2 the heights of two faceted Au clusters on highly oriented pyrolytic graphite (HOPG) determined by STM are plotted versus the gap voltage. A roughly linear decrease is visible and the relative height change is similar for both clusters (Fig. 2b). For the range of gap voltages displayed in Fig. 2 the maximum effect amounts to a few 0.1 nm. Above $V \approx 4\,\text{V}$ the linear trend is interrupted (not shown) due to field emission resonances on the HOPG surface [16,17]. If we assume that at $V \to 0$ the actual geometric height is approached, the measured height leads to underestimated values ($\approx 10\%$ for a typical gap voltage of $V = 2\,\text{V}$). This error is of the same order of magnitude as the uncertainty of the scanner calibration and the accuracy of geometric models applied for the clusters (see Section 3). But if one is interested in accurate absolute numbers a correction of the voltage dependent imaged heights using an extrapolation to zero tunneling voltage according to Fig. 2 would be necessary for each cluster.

In addition to the topographic measurements the scanning tunneling microscope can be operated in the spectroscopy mode for the investigation of electronic properties of the sample system. In this case the lateral position of the tip is kept constant and the tunneling current $I$ is measured dependent on the gap voltage $V$.

![Fig. 2.](attachment:fig2.png)

**Fig. 2.** (a) Measured cluster heights of two individual Au clusters for different gap voltages. Most data points have been measured several times in order to check the reproducibility. (b) The same data as in (a), normalized to the respective linearly extrapolated cluster heights at zero voltage.
The electronic states involved in the tunneling process together with the definition of polarity used here are shown in Fig. 3. For positive sample voltages the unoccupied LDOS is accessed (a) while the occupied states are measured using a negative sample bias (b). For low voltages and assuming constant tip DOS the differential conductivity $\frac{dI}{dV}$ is directly proportional to the local density of states (LDOS) of the sample surface [12]. The set-point $(I, V)$ before starting the spectroscopy procedure determines the signal amplitude according to the condition

$$ I = \int_0^V \left( \frac{dI}{dV} \right)_V dV. $$

(1)

Low voltages and high currents increase the signal-to-noise ratio but they lead to more instable tunneling conditions particularly for clusters.

If the spectroscopy is repeated for several lateral tip locations the resulting data can either be displayed as a set of voltage dependent $\frac{dI}{dV}$ curves or as so-called $\frac{dI}{dV}$ maps. In the latter case the $\frac{dI}{dV}$ values for all locations at a particular voltage are represented by a gray scale image.

In order to improve the signal-to-noise ratio, in this work a lock-in detection method is used instead of the numerical differentiation of the $I(V)$ curves. A modulation voltage with an amplitude of typically $V_{\text{mod}} = 12 \text{ mV rms}$ is added to the tunneling voltage. The corresponding modulation of the tunneling current is detected by a lock-in amplifier which provides directly a d.c. voltage proportional to the differential conductivity $\frac{dI}{dV}$. The normalization constant can be obtained by comparison with the numerical derivative of the simultaneously recorded $I(V)$ curve. We used an active compensation of the cross-talk signal between the modulation voltage and the tunneling current to cancel out the corresponding background signal before the tip is approached to the sample [18].

STS combines high energetic and spatial resolution while $k$ resolution can only be achieved in special sample systems (e.g., standing wave patterns for surface states scattered at defects [19,20]). The energy resolution is given by the thermal broadening of the tip Fermi edge and may be additionally reduced by electronic noise. In our case the resolution
above the temperature of liquid nitrogen \( T = 77 \text{ K} \) is basically determined by the thermal broadening, thus all STS measurements presented in this work were taken at liquid helium temperature \( T_{\text{STM}} \approx 5 \text{ K} \). From \( \mathrm{d}I/\mathrm{d}V \) curves of a superconducting Pb sample at low modulation voltages \( V_{\text{mod}} = 1 \text{ V rms} \) we estimated the energy resolution limited by electronic noise to be \( \sigma_V \approx 5 \text{ meV} \) \[21\]. For the larger modulation amplitudes used in this work we expect an energy resolution of \( \sigma_V = 10, \ldots, 15 \text{ meV} \). The second low-temperature effect is the enhanced stability of the tip and the sample on an atomic scale, which improves the reproducibility significantly.

A complementary method to local STS is angle resolved ultraviolet photoelectron spectroscopy (ARUPS). Within the three-step-model \[22\] the electrons, excited by photons, e.g., from a gas discharge lamp, subsequently propagate through the crystal. If their energy exceeds the work function \( \Phi \) they can escape from the crystal and be detected energetically and angularly resolved with an electron analyzer. Neglecting final state effects (cf. Section 7) the kinetic energy \( E_{\text{kin}} \) of the photoelectron follows the Einstein relation

\[
E_{\text{kin}} = h\omega - \Phi - E_b,
\]

where \( h\omega \) is the photon energy and \( E_b \) is the binding energy of the electron before the photoexcitation. In this work all electron energies are given with respect to the Fermi level \( E_F \) which is set to 0 eV and in correspondence to the positive energy of unoccupied states in STS the occupied states of the photoemission spectra have a negative sign. In general the photoelectron spectrum is proportional to the combined DOS (joint density of states, JDOS) taking into account both, the initial and the final electron state. The signal amplitude is additionally modified according to the transition matrix elements between initial and final states.

Since the focus area of the electron analyzer is typically of the order of some square millimeters the UPS spectra reflect spatially averaged information of the sample properties. The variation of the electron emission angle \( \varphi \), however, provides access to the momentum dependent electronic structure, i.e., the dispersion \( E(k_{||}) \). The parallel component \( k_{||} \) of the momentum vector \( \vec{k} \) can be obtained directly from the kinetic energy and the emission angle because it is conserved when the electron leaves the crystal. In contrast, the perpendicular component \( k_{\perp} \) is changed and for the reconstruction of the entire three-dimensional band structure \( E(\vec{k}) \) it has to be either measured (e.g., by triangulation experiments) or approximated by reasonable models \[22\]. In two-dimensional systems, such as the Shockley surface state (see Section 6), the energy of the electronic states is independent of the wave vector component \( k_{||} \) and the two-dimensional dispersion \( E(k_{||}) \) describes the band structure completely.

In Table 1 the characteristic properties of the methods STS and UPS as used in this work are compared to each other. In particular the combination of both techniques for

<table>
<thead>
<tr>
<th>STS</th>
<th>UPS</th>
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<tbody>
<tr>
<td>High energy resolution at low temperatures ( \Delta E &lt; 10 \text{ meV} )</td>
<td>High energy resolution ( \Delta E &lt; 20 \text{ meV} )</td>
</tr>
<tr>
<td>Local sensitivity on an atomic scale</td>
<td>Averages over some mm(^2) sample area</td>
</tr>
<tr>
<td>Usually no ( k ) resolution</td>
<td>( k_{</td>
</tr>
<tr>
<td>Spectroscopy of occupied and unoccupied states</td>
<td>Only occupied states are accessible</td>
</tr>
<tr>
<td>Limited energy range ( (\approx \pm 5 \text{ V}) )</td>
<td>Energy range limited by photon energy</td>
</tr>
<tr>
<td>Tip DOS may induce artifacts</td>
<td>Spectrum reflects JDOS</td>
</tr>
<tr>
<td>Detection of the surface LDOS</td>
<td>Detection depth ( \approx 1 \text{ nm} )</td>
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</table>
the same sample facilitates a complete characterization of the spatially as well as the momentum dependent electronic structure.

3. Cluster preparation and size dependent cluster morphology

In the following the preparation method used for the cluster samples will be described and the size dependent morphology will be discussed. The clusters are grown by Au evaporation on highly oriented pyrolytic graphite (HOPG) with preformed nanometer-sized pits [23]. The HOPG substrate assures a weak cluster–substrate coupling and can easily be cleaned in UHV. During the cluster growth the pits serve as condensation centers and allow a narrow size distribution, as well as stable imaging conditions in the STM.

In a first step the HOPG crystal is tape cleaved under ambient conditions and subsequently introduced into the UHV chamber. Annealing at a temperature of 600 °C leads to the desorption of the water film and other adsorbates. As the natural defect density is too low for the needed cluster density [23], about \(5 \times 10^2\) surface defects per \(\mu\)m\(^2\) are produced by Ar sputtering at a kinetic energy of 100 eV [24]. Outside the vacuum the defects are oxidized at \(T = 540\) °C to one monolayer deep pits with a diameter of a few nanometers. An atmosphere consisting of 2% O\(_2\) and 98% Ar at ambient pressure is used instead of air to increase the oxidation time to \(t_{ox} \approx 200\) min for a better control. The prestructured HOPG substrates are subsequently reintroduced into the UHV chamber and characterized by STM images. This allows an appropriate choice of the substrate for further experiments (e.g., high pit densities for UPS, whereas for STM/STS lower densities are feasible as well). Fig. 4 shows an overview image of a prestructured HOPG sample. The typical pit diameter is about 10 nm, but also some larger pits with irregular shapes are visible, which are partly coalesced. This is supposed to originate from catalytic etching processes during the oxidation, induced by impurities on the HOPG surface [25]. Nevertheless, these large pits are

Fig. 4. Nanopits (dark areas) on a HOPG surface. A few adsorbates are imaged as bright spots. Image size: 300 nm \(\times\) 300 nm.
not expected to change the growth process significantly because the nucleation starts at step edges rather than in the pit centers (cf. Section 4).

Prior to the metal deposition the samples are again annealed at 600 °C in UHV to remove adsorbates which could serve as unwanted condensation centers. The gold evaporation is carried out with rates between $3 \times 10^{-3}$ ML/s and $1.4 \times 10^{-2}$ ML/s at a sample temperature of $T = 350$ °C using an electron beam evaporator with flux monitor [26]. A small fraction of the evaporant is ionized by the electron beam in the evaporator and accelerated by the high voltage. In order to prevent the creation of additional defects induced by these cations, the sample is biased at an appropriate positive voltage. In this way the cations cannot reach the sample surface and do not lead to a disturbance of the cluster growth. The sample temperature of $T = 350$ °C is chosen to assure a high mobility on the HOPG surface, which facilitates the formation of nearly equilibrated cluster shapes. Significantly higher sample temperatures are avoided because they result in an extremely low condensation coefficient of the gold. By choosing different Au fluxes and evaporation times it is possible to vary the coverage over several orders of magnitude and hence to control the cluster size. The evaporator has been calibrated by adsorbing a sub-monolayer amount of gold onto a Au(111) surface and measuring the area of one monolayer high islands with STM [26]. The cluster density is essentially predetermined by the pit density. We did not find any indication that the cluster growth differs if we divide the evaporation into multiple steps. Details of the growth process and its kinetics are discussed in Section 4.

Subsequent to the metal evaporation the samples were investigated by STM in the same UHV system. As will be shown below, it is also possible to gain information about the cluster morphology from UPS measurements. Some samples, in particular with larger clusters, were prepared for ex situ transmission electron microscopy (TEM) measurements after completing the UHV experiments.

In earlier studies Ag clusters have been investigated using the same preparation and analysis methods [23,24,27,2]. For these samples neither a preferential cluster shape, nor a specific orientation was found. For Ag clusters the UPS spectra were similar to spectra of a polycrystalline Ag crystal and TEM diffraction images exhibited nearly isotropic rings. Au clusters show a different behavior. Our results (cf. also Section 4) indicate a transition of growth mode for clusters of about a few thousands of atoms. Consequently, the description of the morphology is divided into two sections, i.e., “small clusters” with significantly less than $10^3$ atoms and “large clusters”, consisting of at least a few thousand atoms.

3.1. Small gold clusters

Fig. 5 shows the STM image of a Au cluster sample (sample A) with an exposure of about 0.1 monolayers (ML). The clusters are predominantly located at the pit edges, which is clearly visible for larger pits. Whereas the cluster width $d$ is overestimated due to the tip shape, the height $h$ can correctly be determined within a few percent (cf. Section 2). The statistical analysis of several measured cluster heights reveals the average cluster height $\langle h \rangle$ and the standard deviation $\sigma_h$. For the sample in Fig. 5 we get $\langle h \rangle = 1.5$ nm and $\sigma_h = 0.4$ nm based on about 300 different clusters.

For an estimation of the cluster volume, at least the average width to height ratio $\langle d \rangle / \langle h \rangle$ is required. For larger Au clusters it is possible to obtain $\langle d \rangle$ from TEM images, but the diameter of the clusters discussed in this section is near the resolution limit of
the TEM used here. One possibility is to investigate larger clusters and to extrapolate \( \langle d \rangle / \langle h \rangle \) down to the smaller cluster sizes. As will be shown in the next sections, Au clusters change their morphology at a critical size which is still in the range of the TEM resolution. Earlier UPS and STM results for Ag clusters on graphite \([27,29]\) indicate a nearly constant morphology for a broad range of cluster sizes, i.e., no preferential orientation or faceting. For these clusters we find \( \langle d \rangle / \langle h \rangle \approx 1.4 \). In a first approximation we assume that for the small clusters considered here the morphology does not change significantly with the cluster size, i.e., \( d_i / h_i \approx \langle d \rangle / \langle h \rangle \) for each cluster. Two reasonable geometric models for the cluster shape, accounting for the fixed ratio \( d/h \), are shown in Fig. 6. The ellipsoid model would be favored for non-wetting surfaces, i.e., with a metal–substrate interface energy comparable to sum of the respective surface energies. With \( d/h = 1.4 \) the truncated sphere model provides a contact angle of \( 115^\circ \), which is in reasonable agreement with the angle of \( 127^\circ \) determined for \( \mu \text{m} \) sized particles \([30]\). Hence, we favor the truncated sphere model for the following discussion. The volume then can be calculated using

\[
V_{TS}(h) = \pi h^3 \left( \frac{1}{2} \frac{d}{h} - \frac{1}{3} \right).
\]  

Fig. 5. Pseudo 3D image of small Au clusters on a prestructured HOPG surface with larger pits (sample A). The alignment at the pit edges is clearly visible. Image size: 150 nm \( \times \) 150 nm.

Fig. 6. Two possible geometric models for small Au clusters with given height \( h \). Left: ellipsoidal cluster shape. Right: truncated sphere model.
Insertion of $d/h = 1.4$ results in $V_{TS}(h) \approx 1.15h^3$. It is evident that the relative uncertainty of the cluster volume is three times larger than for the height. Assuming that the cluster height can be determined with an accuracy of about 10%, the error of the volume will be 30%. However, this is a systematic error which results, e.g., in an imprecise mean cluster size. For the investigation of systematic trends by comparison of different samples this error is not expected to play a major role. Nevertheless we have to keep in mind that all absolute quantities deduced from the cluster volume, such as the number of atoms per cluster $N$ or the condensation coefficient $\beta$, are influenced by a large uncertainty.

From the cluster volume we get the number of atoms by taking the gold bulk fcc density of 58.9 atoms/nm$^3$. Potential deviations from this value are exceeded by the restricted validity of the geometric model and the accuracy of the height determination. Together with the cluster density $\rho_C$ (i.e., number of clusters per area) deduced from STM or TEM images, the gold coverage $\Gamma_{\text{sample}}$ on the sample and therefore the condensation coefficient $\beta = \Gamma_{\text{sample}}/\Gamma_{\text{evap}}$ can be estimated, where $\Gamma_{\text{evap}}$ is the Au exposure from the evaporator.

Due to the broad height distribution the average volume cannot be deduced using the average height, but the full distribution has to be considered. Inserting the parameters for the height distribution of sample A, we get $\bar{N} \approx 120$ for the most probable cluster size, but the mean value is $\langle N \rangle \approx 280$, and even clusters consisting of more than thousand atoms can be found with the STM.

An increase of the Au coverage results in larger clusters, whereas the number of clusters essentially remains constant (cf. Section 4). A STM image of sample A after an additional Au exposure of about 0.13 ML is shown in Fig. 7 (sample B). In Table 2 the results of the two samples A and B are summarized. Note that the condensation coefficient carries a large error because the systematic absolute uncertainty of 30% is directly transferred to $\beta$.

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**Fig. 7.** Pseudo 3D image of the same sample as in Fig. 5 after an additional evaporation step (sample B). Image size: 100 nm × 100 nm.
3.2. Large gold clusters

At high Au exposures of more than 0.5 ML we observe regular cluster morphologies with flat, almost hexagonal facets on top. Fig. 8 shows a STM image of a cluster sample after evaporation of 0.9 ML gold (sample C). The actual Au coverage on the sample is significantly lower due to the low condensation coefficient $\beta < 1$ (see below).

In the STM image as well as in the line scans the flat facets can clearly be identified (Fig. 8). From several measured images we get an average cluster height $\langle h \rangle = 2.4 \text{ nm}$ with a standard deviation of $\sigma_h = 0.4 \text{ nm}$. Another interesting statistical quantity is the cluster density $\rho_C$, i.e., the number of clusters per area. For the large clusters discussed in this section $\rho_C$ is difficult to determine by means of STM because the probability of tip induced cluster displacement grows strongly with increasing cluster size, leading to underestimated values for $\rho_C$. This experimental difficulty is important in particular for larger image sizes, which would be necessary for a statistically accurate analysis. To overcome these problems, we have applied ex situ TEM for some of the cluster samples after completing the UHV experiments. From the TEM image for sample C (Fig. 9) we deduce a cluster density of $\rho_C = (1390 \pm 70) \mu\text{m}^{-2}$. The error results from the finite number of cluster counts.

---

Table 2

<table>
<thead>
<tr>
<th>Au exposure</th>
<th>Sample A</th>
<th>Sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{\text{evap}} = 0.10 \text{ ML}$</td>
<td>$\Gamma_{\text{evap}} = 0.23 \text{ ML}$</td>
<td></td>
</tr>
<tr>
<td>Cluster density $\rho_C = (1800 \pm 100) \mu\text{m}^{-2}$</td>
<td>$\rho_C = (1600 \pm 100) \mu\text{m}^{-2}$</td>
<td></td>
</tr>
<tr>
<td>Height distribution $h = (1.5 \pm 0.4) \text{ nm}$</td>
<td>$h = (2.1 \pm 0.4) \text{ nm}$</td>
<td></td>
</tr>
<tr>
<td>Number of atoms (TS) $N = 280_{-200}^{+470}$</td>
<td>$N = 700_{-380}^{+400}$</td>
<td></td>
</tr>
<tr>
<td>Condensation coeff. $\beta \approx 0.32$</td>
<td>$\beta \approx 0.35$</td>
<td></td>
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</table>

The number of atoms per cluster was estimated using the truncated sphere (TS) model. The quoted errors are the standard deviations of the respective distributions.

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Fig. 8. Left: STM image of large, faceted Au clusters on HOPG (sample C). Image size: 50 nm $\times$ 50 nm. Right: Line profile through a cluster as marked on the left side.
The orientation of the facets can be determined by TEM diffraction [31] or UPS measurements. Fig. 10 displays an electron diffraction pattern of large gold clusters on HOPG. The most intense ring belongs to the (220) direction, while the (111) ring is much weaker. Additionally, we notice the high index rings (422) and (440) which have already very low intensity for clusters produced by gas aggregation and deposited on the substrate [31]. The high energy electrons in TEM are reflected at the lattice planes almost in grazing incidence. Therefore, only lattice planes perpendicular to the sample surface contribute to

![TEM image of sample C](image1)

Fig. 9. TEM image of sample C (cf. Fig. 8). The Au clusters are visible as dark spots on the bright background of the HOPG substrate. Image size: 540 nm × 540 nm.

![Electron diffraction pattern](image2)

Fig. 10. Electron diffraction pattern of large Au clusters on HOPG. The observed (220), (422), and (440) rings belong to lattice planes perpendicular to the (111) direction. Data from Ref. [31].
the diffraction pattern. The (220), (422) and (440) diffraction rings are the first three belonging to lattice planes perpendicular to the (111) plane. This shows that the clusters are oriented with their (111) plane parallel to the HOPG (0001) surface. The occurrence of diffraction rings instead of discrete spots points to a random lateral orientation. The investigation of the lateral orientation by STM images of faceted Au clusters also does not favor a particular lateral direction.

The diffraction measurements have to be done ex situ which is cumbersome and destructive due to the necessary sample thinning procedure and the transport under ambient conditions. However, the distinction of different orientations is also possible by using in situ UPS measurements. The d-band photoelectron spectrum of another cluster sample (sample D) in normal emission is shown in Fig. 11a. For this sample we used similar preparation parameters as for sample C (see Section 6 for details). The extraction of the Au signal is done by subtracting the corresponding spectrum of the bare HOPG substrate (see Fig. 11b). This is justified because the relative projected area of the clusters for all samples is below 10%. For the larger clusters we introduced a weighting factor, i.e., we subtracted only a fraction of the HOPG intensity to account for the increased Au covered

![Graphs showing UPS spectra](image)

Fig. 11. (a) UPS spectra of the Au d-band structure for sample D with about 1.3 ML evaporated Au. Solid curve: measured spectrum of the cluster sample. Dashed curve: spectrum of the bare HOPG substrate. (b) Difference signal of the two spectra in (a). (c) UPS signal of a polycrystalline gold sample. (d) UPS signal of a Au(111) single crystal. Note the similarity to (b).
area. The weighting factor was adjusted such that the prominent HOPG structure at $E \approx -8.5$ eV vanishes in the difference spectrum.

The comparison of the cluster spectrum with spectra of a bulk Au(111) surface and a polycrystalline gold sample, respectively, gives evidence for the (111) orientation of the cluster facets. In this way the normal emission UPS d-band spectrum can be used as a fingerprint to identify the crystal orientation.

Though the overall cluster shape is strongly modified by the tip geometry, the facet shape and its area can be determined correctly from the images (cf. Fig. 1). The facet shapes could be classified into four different types which are shown in Fig. 12. Type I and II display a symmetry which is in accordance with the expected shapes for a small fcc crystallite while type III and IV cannot be identified with a corresponding equilibrium morphology [26]. This points to cluster coalescence during the growth process.

We have measured the cluster height as well as the facet area $\Omega$ for more than 100 clusters on sample C. In Fig. 13 the corresponding diameter $d_\Omega = 2\sqrt{\Omega/\pi}$ of a circle with the same area $\Omega$ is plotted versus the cluster height. It is remarkable that we could not find any faceted clusters below a cluster height of about 1 nm. We emphasize that despite the faceting the cluster morphology is still three-dimensional. This becomes evident by the combination of STM and TEM of the same sample. The average lateral cluster diameter from the TEM data is $\langle d \rangle = 5.1$ nm. Together with the STM results for the heights we obtain $\langle d \rangle / \langle h \rangle = 2, \ldots, 3$, in contrast to other, more two-dimensional systems like Ag/Ag(111) ($\langle d \rangle / \langle h \rangle \approx 40$) [32] or Pd/Al2O3 ($\langle d \rangle / \langle h \rangle \approx 5$) [33].

To obtain a more complete view of the three-dimensional cluster morphology we additionally used geometric models. Knowing the (111) orientation of the top facets, a reasonable model for the large gold clusters is a truncated octahedron [26], which corresponds to the closed-packed fcc lattice. The volume of a truncated octahedron with given height $h$ and facet area $\Omega$ (Fig. 14) evaluates to

$$V_{TO} = 0.217 \cdot h^3 + 0.987 \cdot h^2 \sqrt{\Omega} + h\Omega.$$ \hfill (4)

In many cases the facet shape of the measured clusters deviates from the perfect hexagon. Nevertheless, the calculated cluster volume is exact within a few percent, which has been checked by calculating explicitly the volume of an asymmetric “octahedron” for the clusters with most asymmetric facets [26].

![Fig. 12. The four different facet types observed for large Au clusters on HOPG. See text for details.](image)
Alternatively, the facet can be approximated by a circle, leading to a truncated cone for the cluster morphology [34]. The apex angle is chosen to be 60°, which is a reasonable approximation for the (111) and (100) side facet angles of 70.5° and 54.7°, respectively.

The cluster volume is then

\[ V_{TC} = \frac{0.349}{3} \cdot h^3 + 1.023 \cdot h^2 \sqrt{\Omega} + h\Omega, \]

which differs only a few percent from the octahedron volume for our samples. With these geometric models we can evaluate the number of atoms for each cluster solely using STM data. As a consequence, the entire deposited Au amount \( \Gamma \) and therefore the condensation coefficient \( \beta \) can be estimated by summing up the volume of all clusters in a certain sample area. A summary of the distribution of measured facet areas and cluster sizes for sample C is given in Table 3. The discussion will be continued using UPS data and introducing a growth model in the next section.

Fig. 13. Facet diameter \( d_\Omega \) versus cluster height \( h \) of 104 faceted Au clusters on sample C, determined by means of STM. The open circles indicate clusters with facets of type III or IV (cf. Fig. 12). Their large facet area and asymmetric facet shape can be explained by coalescence processes. The straight line \( h_{\text{min}}(d_\Omega) \) roughly defines a lower limit for the observed cluster heights in dependence on the facet diameter. The crosses indicate clusters grown in pits with a depth of more than 1 ML, therefore their height, measured with respect to the surface, is underestimated. From Ref. [26].

Fig. 14. Truncated octahedron model for the morphology of faceted Au clusters. From Ref. [26].
4. STM and UPS study of the growth process

In the previous section we divided the discussion of the cluster morphology into two parts: for small, non-faceted clusters we used a truncated sphere model, whereas for large, faceted clusters the truncated octahedron model was favored. In this section the growth process will be discussed in more detail based on combined STM and UPS results, starting from a few adatoms, undergoing the mentioned morphology transitions, until approaching crystal equilibrium shapes.

4.1. Nucleation centers

During the deposition the metal atoms adsorb on the substrate and form a two dimensional phase of diffusing particles [35] until they either condense to clusters or finally desorb again (see also Fig. 22 below). The key role of the nanometer sized pits on the HOPG substrate is to provide appropriate condensation centers which capture the metal atoms and hence serve as starting locations for subsequent nucleation processes. In the STM images we observe clusters at the edge of the pits as well as at monoatomic HOPG steps. Thus graphite sites with low coordination number are apparently preferred for the cluster growth. Once a critical nucleus has developed, the probability of the formation of further nuclei in its vicinity is much lower than the capture of additional atoms, resulting in a growth of the existing cluster. The cluster density \( q \), i.e., the number of clusters per area remains essentially constant during the growth, even if the pits are large enough to allow the formation of several clusters at their edges. The constant cluster density can be checked by STM measurements of the same substrate after each evaporation step. Fig. 15 shows an overview image of sample B and sample C. The preparation parameters of these samples were presented in the last section. For the right image the gap voltage was set to 10 V in order to increase the tip–sample distance for a lower probability of tip induced cluster movement. According to the discussion in Section 2 the cluster heights are largely underestimated due to this high voltage, but this is of minor interest in this context. The number of clusters has not changed drastically, though the gold exposure \( \Gamma_{\text{evap}} \) of sample C was increased by a factor of 4 with respect to sample B and the ratio of the actual Au coverages \( \Gamma_{\text{sample}} \) on the samples is even larger.

The probability for a gold atom to be captured by an existing nucleus is not equal to 1. This means that the condensation coefficient \( \beta = \Gamma_{\text{sample}}/\Gamma_{\text{evap}} \) is lower than 1, as already estimated from the STM images in the last section. If the mean adatom diffusion length \( \lambda_{\text{diff}} \) before desorption, as discussed below, is much larger than the typical cluster–cluster
distance, the condensation coefficient will approach 1. At $T = 350 \, ^\circ$C the diffusion length is about $\lambda_{\text{diff}} \approx 6 \, \text{nm}$ [36], which is in our case lower than the most cluster distances (see, e.g., Fig. 9). As a consequence, a low value of $\beta$ corresponds to a small influence of neighboring clusters on the growth. This is confirmed by the fact that no significant correlation could be found between the local cluster density and the corresponding sizes: if the diffusion length was large compared to the cluster distances, clusters close to each other would share the diffusing atoms in the same area, which would lead to smaller sizes than for areas with a low cluster density. Hence, for the further investigation of the growth process it is sufficient to reduce the problem to the growth of a single cluster, neglecting the influence of the surroundings.

### 4.2. Cluster location

In this section we will analyze in a first step the exact lateral location of the Au clusters with respect to the nanopit edges. In other words, we would like to distinguish between the growth on the bottom of the pit and on the top plane of the HOPG substrate. Usual STM images as e.g., Fig. 5 are not well suited for this problem because of the unknown influence of the tip on the cluster morphology. Assuming a symmetric lateral morphology, the highest point of the imaged cluster corresponds to its center, independent of the tip shape. But the exact location of the pit edge below the cluster is not known and due to the curved pit shape with kinks and edges a simple interpolation of the pit through the cluster is not possible.

To overcome this problem we make use of an otherwise unwanted effect, the displacement of single clusters from their sites induced by lateral tip–cluster forces. In Fig. 16 two STM images of the same sample area are shown before (a) and after (b) the tip induced cluster movement. The two lower clusters in Fig. 16a are missing in the second image (b). Fitting the pit contour of image (b) to the corresponding visible part of (a) the lateral cluster location can be reconstructed. The result is shown in Fig. 17, together with the expected true cluster diameter according to $d/h = 1.4$. The centers of the clusters are located very close to the pit contour, i.e., each cluster is grown partly on the upper and
partly on the lower graphite plane. We have verified this finding for 15 other clusters which were displaced between two STM scans.

The cluster location is probably not determined predominantly by the growth dynamics. Instead we assume that the location as well as the morphology will be basically given...
by the minimization of the overall energy. This is consistent with the formation of well defined facets for larger clusters and means that the position at the pit edge is one aspect of the equilibrium state. For Au clusters with a diameter in the micrometer range it is well known that the time which is necessary to reach the equilibrium shape is of the order of a few days, even if the temperature is chosen to be just below the melting point [37]. During the preparation of our gold clusters the temperature of $T = 350 \, ^\circ C$ is kept for only a few minutes before cooling down the sample. In order to check if this is enough for clusters with a diameter of a few nanometers we estimate the order of magnitude of the relaxation time for the equilibrium shape using a formula which is derived in Ref. [38] and used in Ref. [37] for Au crystals with micrometer dimensions:

$$\tau = \frac{r^4 kT \sigma}{24\gamma D_v v^2}, \quad (6)$$

where $r$ is the cluster radius, $k$ is Boltzmann’s constant, $\gamma$ is the surface energy ($\approx 1 \, J/m^2$ [39]), $D_v$ is the surface diffusivity ($\approx 10^{-15} \, m^2/S$ [40]), $v$ is the atomic volume (1.7 $\times$ 10$^{-29}$ m$^3$ for Au), and $1/\sigma$ is the number of atoms per surface area (7 $\times$ 10$^{-20}$ m$^2$). The formula is based on the assumption that the shape is in first order described by a sphere and that surface diffusion is the dominating mechanism for morphology changes. Depending on the cluster size, we get relaxation times between $\tau \approx 10^{-4} \, s$ (for $r = 1 \, nm$) and $\tau \approx 10^{-2} \, s$ (for $r = 4 \, nm$). This means that the time used for the cluster growth is several orders of magnitude longer than the relaxation time, therefore we expect essentially the formation of equilibrium shapes of the cluster/surface system. For well defined crystalline surfaces, however, additional effects may occur which increase the relaxation time, such as the Ehrlich–Schwoebel barrier [41–43]. The location of the nucleation centers at the pit edges indicates a potential minimum for diffusing Au atoms at these sites. In view of the equilibrium state the cluster tends to maximize the number of atoms in contact with these low energy sites. As a consequence, the cluster center will approach the pit edge, in agreement with our STM analysis.

For the cluster volume determination we measure the cluster height with respect to the upper HOPG plane. With the analysis of this section the height is systematically underestimated by 0.35 nm (one layer of HOPG) on a part of the cluster basis. This results in an error of the volume which ranges from less than 10% for samples C and D up to about 15% for the small clusters of sample A. Thus this error may be neglected compared to the systematic error of the volume determination of about 30% (see last section).

4.3. Photoemission study of the growth process

The investigation of the growth process consisting of several evaporation steps is difficult to realize by means of STM. Besides the time consuming counting procedure and the instable imaging of larger clusters, the sample has to be transferred into the STM after each evaporation step. Under these circumstances it is hardly possible to guarantee the sample cleanliness for a large number of evaporation steps which is necessary in order to avoid influences of adsorbates on the growth process. Therefore we decided here to study the cluster growth solely by UPS. It is clear that therefore all results are based on average information on the inhomogeneous sample. The distribution of quantities like the cluster size is not taken into account explicitly, but we henceforth focus on the respective mean values.
The overall photoelectron intensity from the Au 5d-electrons can serve as a measure for the actual coverage $I_{\text{sample}}$ on the sample and hence for the condensation coefficient $\beta = I_{\text{sample}}/I_{\text{evap}}$. Since the cluster density $\rho_C$ remains essentially constant, the coverage is expected to increase with the average cluster volume $V$. However, the quantitative analysis of intensities is not straightforward, mainly due to the finite escape depth of the photoelectrons in the material.

The HOPG substrate used for the UPS experiments is shown in Fig. 18a. The surface consists of extremely small, but quite monodisperse nanopits. The number of pits per area is about $q_{\text{pits}} \approx 1300 \text{ \mu m}^{-2}$ and we expect the formation of one cluster per pit for this sample, resulting in the same cluster density $\rho_C$. For STM measurements the cluster sample after the Au evaporation is not well suited because the small pits provide a smaller contact area between HOPG edges and clusters than the previous samples. Hence the probability for tip induced displacement is significantly increased and stable images are difficult to obtain.

The Au evaporation was carried out at $T = 350^\circ C$ in analogy to the previous samples. We divided the evaporation into six steps, changing the respective exposure such that in each step $i$ the total Au exposure $I_{\text{evap}}^i$ (i.e., the sum over all previous evaporation steps) is increased by a factor of $I_{\text{evap}}^i/I_{\text{evap}}^{i-1} \approx 2.3$. Thus, the evaporated gold amount was changed in constant steps on a logarithmic scale, starting from $I_{\text{evap}}^1 = 0.04 \text{ ML}$ up to $I_{\text{evap}}^6 = 2.8 \text{ ML}$. After each step the sample has been cooled down to room temperature and the UPS measurement was started.

Subsequent to the UPS study we tried to apply STM for the largest clusters ($I_{\text{evap}} = 2.8 \text{ ML}$), but it was only possible to achieve a rough estimation about the cluster heights and it was extremely difficult to image larger sample areas, such as shown in Fig. 18b. The figure is dominated by the displacement of several clusters during the scan, only a fraction of the clusters could be imaged successfully. The cluster height ranges from $h \approx 3 \text{ nm}$ up to $h \approx 7 \text{ nm}$ and we estimate the average height to $\langle h \rangle \approx 5 \text{ nm}$. The cluster density is consistent with the pit density of Fig. 18a.

Fig. 18. (a) STM image (300 nm × 300 nm) of the substrate of sample E, which was used for the UPS experiment. Several pits are only visible as bright spots because of their small diameter. (b) Pseudo 3D image (200 nm × 200 nm) of the same sample after the last evaporation step ($I_{\text{evap}} = 2.8 \text{ ML}$).
First we focus on the Au 5d-band structure at the energy of $-7\,\text{eV}, \ldots, -2\,\text{eV}$ with respect to the Fermi level. In Fig. 19 normal emission spectra at $T = 300\,\text{K}$ with low angular resolution ($\pm 8^\circ$) are shown for the lowest and the highest Au coverage, respectively. The HOPG substrate signal has been measured before under the same conditions and is subtracted in order to extract the Au signal (cf. Fig. 11). For each spectrum the Fermi energy was determined separately on a tantalum foil. Whereas the spectrum for the small clusters contains only two broad peaks, the large clusters in the right part of Fig. 19 exhibit all essential structures of the bulk Au(111) surface.

Another striking difference is the intensity ratio between the first feature at $-6\,\text{eV}$ and the second one around $-4\,\text{eV}$, which has not reached the bulk value even for the largest clusters with several $10^4$ atoms (cf. the low temperature spectrum in Fig. 11d; the ratio does not change significantly at $T = 300\,\text{K}$). For possible origins of this effect one might think of the energy dependence of the electron escape depth $\lambda$, since the electron energies of the two features differ by $\approx 2\,\text{eV}$. This effect is expected to be most relevant for small clusters, because then the intensity is proportional to the cluster volume, independent of $\lambda$. In contrast, the bulk intensity is proportional to $\lambda$. Therefore, an upper limit for the relative change of the intensity ratio is given by $\lambda(17.5\,\text{eV})/\lambda(15\,\text{eV})$, according to the kinetic energy of the electrons for the two structures. The use of a semi-empirical formula for $\lambda(E_{\text{kin}})$ [44] yields an upper limit for relative difference of about 25%, which is evidently lower than the observed change. As a result, the increase of the relative intensity of the first structure at $-6\,\text{eV}$ can only partially related to the electron escape depth. More likely, the UPS data indicate a change of the actual electronic band structure. This is consistent with the expected size of less than 100 atoms for the small clusters in Fig. 19 (left part). For such small Au particles theoretical and experimental investigations for free clusters [45] as well as photoemission experiments on supported clusters [46] indicate deviations from the bulk behavior. A direct theoretical comparison of the density of states between large metal clusters and the bulk material is given in Ref. [47] for the case of copper. But also the con-

![Fig. 19. Photoelectron spectra after subtraction of the HOPG background (cf. Fig. 11) for the lowest (left) and the highest (right) gold exposure used in the experiment. The evaporation was done at $T = 350\,\text{C}$, whereas the measurement was performed at room temperature.](image-url)
tribution of the side facets of the clusters with other orientations than the (111) facets on top will lead to size dependent differences as compared to the bulk (111) surface.

The evolution of the d-band structure for all Au coverages is shown in Fig. 20a. Note the logarithmic scaling which is used in order to allow a quantitative representation of all spectra in a single plot. The relative intensity of the first peak at $-6$ eV increases gradually. In contrast, the fine structure at about $-4.5$ eV, which is typical for a (111) surface (cf. Fig. 11), appears quite suddenly at an exposure around 0.5 ML. With regard to the STM measurements for sample B (Fig. 7) and sample C (Fig. 8), the occurrence of the (111) fine structure is in coincidence with the formation of the hexagonal facets discussed in Section 3. This gives further evidence for a transition of the cluster morphology to well defined crystallites at $I_{\text{evap}} \approx 0.5$ ML.

The morphology change is also confirmed by UPS measurements near the Fermi level with high angular resolution ($\pm 1^\circ$). In Fig. 20b the peak of the Shockley surface state (cf. Section 6) occurs at $I_{\text{evap}} \approx 0.5$ ML, in analogy to the Au(111) fine structure of Fig. 20a. Since a well defined (111) surface is necessary for the formation of a Shockley surface state, this behavior is not unexpected.

For the following discussion we focus on the evolution of the overall intensity of the d-band spectra of Fig. 20a. The structural change, as well as the mentioned change of the

![Fig. 20.](image)

(a) Background corrected UPS results for six different gold exposures for sample E on a logarithmic scale. The Au d-band intensity varies over more than two orders of magnitude. The non-vanishing signal above the Fermi level is caused by satellites in the HeI radiation line. (b) Normal emission photoelectron spectra with $\pm 1^\circ$ angular resolution for the region near the Fermi level after subtraction of the HOPG background. For $I_{\text{evap}} \geq 0.5$ ML the surface state peak is clearly observable. The spectrum for the lowest coverage ($I_{\text{evap}} = 0.04$ ML) is not shown because of the poor signal-to-noise ratio.
intensity ratio between the two main features is not taken into account. Instead, we assume that the integrated intensity is a measure for the Au quantity on the sample. This simplification is tolerable because we are interested in the growth process on a semi-quantitative level. The cluster size dependent change of the UPS d-band spectra will certainly affect the extracted Au quantity, but the errors are expected to remain in the range of a few percent. The intensity change of the first structure at $-4$ eV, probably one of the largest error sources, result in an underestimated intensity integral of $\approx 10\%$ for the smallest clusters. For the following analysis such deviations are not relevant.

In Fig. 21 the integrated 5d peak intensities are shown in a double logarithmic plot for all six Au coverages of sample E (full circles). The summation is performed over the d-band region ($-7$ eV, $\ldots$, $-11$ eV) of the background corrected data in Fig. 20a. The data points can be fitted quite accurately by a straight line with the slope $m = 1.19 \pm 0.03$, corresponding to the power law

$$I(I_{\text{evap}}) = c \cdot \left(\frac{I_{\text{evap}}}{1\ \text{ML}}\right)^m,$$

where $I$ is the integrated photoelectron intensity and $c$ is the intensity at $I_{\text{evap}} = 1\ \text{ML}$.

The fact $m > 1$ cannot be explained due to the effect of the electron escape depth $\lambda$, because this would decrease the signal for larger clusters, and so lead to a slope $m < 1$. Therefore the stronger than linear increase of the photoemission signal clearly points to a condensation coefficient $\beta$ which increases with the coverage. This is in agreement with the results from the STM measurements in Section 3 (cf. Tables 2 and 3), and can be explained with the microscopic kinetic model developed in Refs. [35,36]. The basic processes considered in this model are shown in Fig. 22.

The atoms arrive at the surface either on an existing cluster (direct impingement) where they are adsorbed with probability 1, or they are adsorbed on the substrate between the clusters, where they diffuse in a random walk. In the latter case they either desorb again after moving a mean length before desorption $\lambda_{\text{diff}}$ or they are captured by an existing

![Fig. 21. Double logarithmic plot of the integrated d-band UPS intensity versus the evaporated Au amount for sample E (symbols). The thin solid line is the linear fit for sample E. The dashed line corresponds to a linear function, i.e., peak area $\propto I_{\text{evap}}$. Both curves are shifted arbitrarily in the vertical direction.](image-url)
cluster. In this way the probability for sticking increases with the clusters growing larger. One can use this model to explain the observed increase of the condensation coefficient in our experiments. This analysis includes the effect of the electron escape depth for the signal intensity [48]. But since many of the required parameters like the diffusion length before desorption $\lambda_{\text{diff}}$ or the size dependent morphology (described, e.g., by $d/h$) are not known with a high quantitative accuracy, the analysis remains on a qualitative level. In addition non ideal experimental conditions complicate the modeling as, e.g., potential deviations from the perfect statistical distribution of nucleation centers (particularly for large pits) or the diffusion along monoatomic steps or pit edges.

However, the essence of this section is the observation of a condensation coefficient increasing with the clusters growing larger, together with the plausibility check using a simple growth model. For controlled preparation of samples with a certain cluster size the observed change of the condensation coefficient with the coverage has to be taken into account.

Another important conclusion of this section is that with our typical sample parameters for the number of nucleation sites per area, the cluster size and a sample temperature of 350 °C during cluster growth, $\lambda_{\text{diff}}$ has to be significantly smaller than the mean cluster–cluster distance. Otherwise the condensation coefficient would be close to 1. Therefore the other surrounding clusters have only a minor influence on the growth process, which is of advantage to obtain a narrow cluster size distribution. This will be of crucial importance, e.g., for the experiments described in Section 8.

5. Electronic structure of small clusters

The topographic imaging of smaller, non faceted clusters is in general easier than for the large clusters. The probability for tip induced cluster displacement is significantly reduced, allowing larger image sizes and therefore more efficient measurements. However, for scanning tunneling spectroscopy on single clusters the situation is different. While the flat top facets of large clusters enable stable tunneling conditions for several hours, in absence of a facet residual lateral forces are hardly avoidable. In particular during the
spectroscopy process this can lead to a displacement of the cluster. For this reason it is crucial to locate the tip exactly on top of the cluster center, i.e., the highest position in the topograph. Unfortunately this is a challenging task due to drifts induced thermally or by the STM piezo crystals [49].

Earlier STS studies for platinum or silver clusters exhibited prominent structures in the $dI/dV$ curves [2,50]. Although a tendency to lower peak distances for larger clusters is observable, a systematic size dependence of the peak positions is not evident from these data. In the corresponding study of small gold clusters presented here we focused on systematic trends in a large number of measurements performed on individual clusters.

In Fig. 23 the averaged $dI/dV$ curves for 61 different clusters are summarized. They are arranged by the cluster height and normalized to the same amplitude. For each Au cluster we took about 10 $dI/dV$ curves and only if they were identical within the signal-to-noise ratio they were accepted and averaged. At first glance the richly structured spectra seem to show hardly any systematic behavior. However, for certain height ranges the curves exhibit striking similarities or systematic trends (thick curves). The curves indicated with

![Figure 23](image)

Fig. 23. Averaged $dI/dV$ curves of 61 different small, non faceted Au clusters on HOPG. The spectra have been taken in arbitrary order and then arranged in the plot by the corresponding cluster height. Hence the cluster heights are not equidistant. Systematic trends are indicated by thick lines. The spectra marked with “m24” and “m34” are measured on the same cluster (see text).
“m24” and “m34” illustrate the reproducibility of the spectra. The same cluster ($h = 1.6$ nm) was measured twice, some hours apart, with several tip preparation steps in between (i.e., voltage pulses or controlled tip–sample interactions at a different sample position). The two $dI/dV$ curves are almost identical, except for the sharp peak around $-1$ V which has shifted to lower energies. This fits well into a more general observation: we could distinguish between two different types of structures. On the one hand we observe quite sharp peaks, which are dependent on the actual tip condition as well as on the exact lateral position on top of the cluster (cf. also e.g., Ref. [2]). The position dependent shifts are typically of the order of a few 10 meV. The other, mostly broader structures seem to represent more intrinsic properties of the cluster/surface system.

The theoretical description of the observed structures is extremely difficult. Different effects could in principle contribute to the $dI/dV$ curves. First, in the limit of a very few atoms one would expect a discrete DOS arising from the molecular electronic levels. Calculations based on a parameterized tight binding model for free Cu-clusters indicate a transition to a continuous DOS at about 100 atoms [47]. The average number of atoms for the clusters of sample A is about $N = 280$ (cf. Table 2), thus the observation of discrete molecular states may appear to be improbable. In the limit of non-degenerated (except for the spin degeneracy) electron states the mean energy spacing near the Fermi edge would be [2].

$$\delta E = \frac{2\pi^2 \hbar^2}{(mk_F V)}, \quad (8)$$

where $m$ is the electron mass, $k_F$ is the Fermi wave vector, and $V$ is the cluster volume.

In the case of highly symmetric particles, however, the multiple degeneracy enlarges the mean level distance. In analogy to the electronic shell structure of alkali clusters [51,52] peaks in the DOS correspond to shell closings at so-called “magic” cluster sizes. For a spherical metal particle the electronic structure can be calculated using self-consistent jellium techniques [53] or semiclassical approaches [54] developed originally by Gutzwiller [55] and Balian and Bloch [56]. In a simple periodic orbit approach the mean length $\langle L \rangle$ of classical orbits determines the main shell oscillation periodicity. For a spherical cluster of the radius $R$ one gets $\langle L \rangle = 5.42R [53]$, which results in an energy spacing of [2].

$$\Delta E = \hbar^2 k_F \pi/(2.71mR). \quad (9)$$

These main shell closings for high symmetry particles give an upper limit for the observed peak distances. In Fig. 24 the two limits for Au clusters according to Eqs. (8) and (9) with $k_F = 1.2$ Å$^{-1}$ are shown together with the area of measured peak distances estimated from Fig. 23. Since the experimental energy spacing remains within the two limits, the interpretation in terms of discrete, partly degenerated electron states is plausible. This is supported by the striking similarities and systematic trends of spectral features in Fig. 23 (thick curves) for different individual clusters of similar heights, particularly around $h \approx 1.1$ nm, $h \approx 1.4$ nm, and $h \approx 1.67$ nm, respectively.

A direct quantitative comparison between theory and experiment is not feasible due to the imperfect knowledge of the cluster size and morphology. Even if we knew the exact position of every Au atom the calculation of the electronic structure would be extremely complex due to the large number of atoms and the specific properties of Au, as e.g., large relativistic effects [57,45]. In a bulk-like approach the application of the semiclassical methods mentioned above would require the analysis of periodic orbits taking into account the anisotropic electron band structure of gold and potentially the formation of facets as discussed in Ref. [58].
Another possible effect is connected to the experimental setup. The tunneling current is not solely dependent on the electronic structure of the cluster, but the physics of the entire tip/cluster/surface system has to be taken into account. If the cluster–substrate interaction is low the system corresponds to a double-barrier tunnel junction (DBTJ) [59]. It consists of a metal island coupled to two electrodes via tunneling junctions. The equivalent circuit diagram and the corresponding setup during our experiment are shown in Fig. 25.

The expected $I–V$ curves can be calculated with rate equations [60] which can be easily solved numerically. Their detailed shape depends strongly on the choice of the capacitances $C_{1,2}$ and the resistances $R_{1,2}$, but typical curves exhibit step-like features as shown in Fig. 26. These steps are caused by single electron charging of the island and they would

![Fig. 25. Circuit diagram of a double barrier tunnel junction (left). In the STM setup (right) $R_1$ and $C_1$ correspond to the tunneling path between tip and cluster, whereas the electron transport from the cluster into the substrate is determined by $R_2$ and $C_2$.](image-url)
lead to peaks in the differential conductivity $dI/dV$. For certain ranges of the parameters the $I–V$ curves consist essentially of a sum of equally spaced and thermally broadened steps. In the limit $R_1 \gg R_2$ and $C_1 \gg C_2$ the step distance is given by $\Delta V = e/C_1$. The energetic positions of the steps and the width of the “Coulomb blockade” (i.e., the region with zero current at low voltages) is dependent on the offset charge $Q_0$ on the cluster which can be induced by work-function differences [60]. From typical tunneling distances of about 0.5 nm and cluster sizes of a few nm we estimate the capacitance between cluster and tip to be about $C_1 \approx 10^{-19}$ F which would lead to $\Delta V \approx 1$ V. This is significantly more than the observed peak distances in the $dI/dV$ spectra in Fig. 23. It is difficult to estimate the capacity $C_2$, if there would exist a significant barrier for the tunneling current. But as pointed out above, we can distinguish between two different kinds of STS peaks, and possibly the sharp ones are connected to the influence of the DBTJ. This is in agreement with the fact that these sharp peaks depend on the lateral tip position [2] as well as on the tip condition (see Fig. 23). However, a quantitative analysis would require a systematical investigation of the Coulomb effect, e.g., by varying the tip–cluster distance and hence the parameters $R_1$ and $C_1$. This is very difficult because the tunneling current changes by about an order of magnitude, if the distance is changed by 0.1 nm [10]. Therefore it would require stable STS measurements on the same cluster for a broad range of different tunneling parameters without changing the tip shape.

Although we have discussed different mechanisms leading to a peak structure in the differential conductivity for small clusters the observed features in the $dI/dV$ spectra of small Au clusters on HOPG cannot be finally explained on a quantitative level. Due to the undefined morphology as compared to large, faceted Au clusters the systematic investigation of the electronic structure is difficult. A promising approach is the utilization of an alternative preparation method, the controlled deposition of size-selected clusters under soft-landing conditions [61,62]. The well defined and tunable cluster sizes would reduce the morphology uncertainty and thus facilitate more targeted measurements. In addition the direct

![Graphs of I-V and dI/dV curves](image-url)
comparison to the electronic properties of free Au clusters is possible. Such experiments are the topic of future projects [63].

Recently, a self-consistent theoretical approach based on an approximation of density functional theory was used to compare the differential conductance and the density of states for silver clusters on graphite with less than 100 atoms [64]. Experimental STS data for well defined cluster–surface systems will allow a more direct comparison with such detailed theoretical modeling. We expect that this will help to extract the effect of the cluster–surface interaction, even if the experimental control of the tip configuration will still be difficult.

6. Electronic structure of large clusters

As demonstrated in Sections 3 and 4 the cluster morphology changes from smaller clusters with more undefined shapes towards larger, faceted clusters with well defined crystal orientation. The electronic structure is expected to be significantly influenced by the morphology. Hence, for a correct interpretation of the experimental spectra the knowledge of geometric details will be crucial. In particular for large, faceted Au clusters on graphite this precondition is well fulfilled and a description in view of bulk properties is expected to be appropriate. As shown in Section 5 the situation is more complex for smaller clusters, for which the concept of well defined crystal structures and surfaces breaks down.

The experimental methods described in Section 2 allow investigating the electronic structure of metal and semiconductor surfaces. One of the most prominent features of the (111) surfaces of noble metals is the Shockley surface state [65]. In the course of this section Shockley surface states will be important for the interpretation of the experimental results. Simple models are sufficient to reproduce the experimentally determined surface-state properties at least qualitatively. For a detailed discussion the reader is referred to, e.g., Refs. [65–68].

Basically the two dimensional surface state is formed by a confinement of electrons perpendicular to the surface—on the one side by the vacuum barrier and on the other side by a band gap in the surface band structure. Parallel to the surface the electron propagation is not constrained, thus the surface state can be treated as a two-dimensional free electron gas. In a parabolic approximation the surface state is fully characterized by the energy onset $E_0$ and the effective mass $m^*$. The density of states for the surface state is then a step function, zero below $E_0$ and constant above.

In the present section we give an overview of the experimental results and the analysis for large gold clusters published in Refs. [34,69]. In Section 8 the discussion will be refined, joining the results of the different experimental techniques.

The occurrence of (111) top facets justifies the treatment of the clusters as small single crystallites. In this view the electronic structure is described by the bulk lattice, with additional consideration of the reduced size. However, it is not clear a priori that the properties of a Au crystal are reflected quantitatively by clusters with dimensions of about $25 \times 25 \times 25$ atoms or lower. Besides the geometry also the cluster–surface interaction is expected to exert an influence on the electronic system. Due to the weak coupling between Au and the HOPG surface this effect is neglected in a first step.

Two overview images of the cluster sample discussed exemplarily in this section (sample D) are given in Fig. 27: the TEM image visualizes the lateral arrangement of the clusters and the STM topograph reveals their morphology in more detail. In Fig. 27b the forma-
tion of nearly hexagonal top facets is evident, as discussed in Section 4. The mean cluster height for this sample is \( \langle h \rangle = 2.9 \text{ nm} \) and typical facet areas are about \( \Omega \approx 40 \text{ nm}^2 \). The Au exposure was about \( \Gamma_{\text{evap}} = 1.3 \text{ ML} \), but the uncertainty is rather high compared to the other samples of this work because the evaporator calibration was extrapolated for another set of evaporator parameters. A comparison of the UPS spectra with the analysis in Section 4 suggests a larger exposure around \( \Gamma_{\text{evap}} \approx 1.8 \text{ ML} \).

### 6.1. Scanning tunneling spectroscopy

First we focus on a cluster with a height of \( h = 3.9 \text{ nm} \) and a facet area of \( \Omega = 37 \text{ nm}^2 \) (Fig. 28). It exhibits a facet shape corresponding to type II of Fig. 12 and the truncated octahedron model results in a cluster size of \( N = 1.5 \times 10^4 \) atoms.

![Fig. 27.](image1)  
(a) TEM image (540 nm × 540 nm) of sample D. (b) 3D display of a STM image (100 nm × 100 nm) for the same sample. Note the regularly shaped top facets on the larger clusters.

![Fig. 28.](image2)  
3D STM image (40 nm × 40 nm) of a faceted Au cluster on sample D. The cluster height is \( h = 3.9 \text{ nm} \) and the facet area \( \Omega = 37 \text{ nm}^2 \). The 2D facet silhouette is shown in the inset of Fig. 29.
The flat facets facilitate very stable tunneling conditions on top of the clusters. In Fig. 29 we present $dI/dV$ data taken on the top facet. We compare spectra measured in the center of the cluster facet and spectra averaged over the complete area of the facet. For selected voltages we present $dI/dV$ maps, which show pronounced patterns with nodes and antinodes, arranged in the approximately hexagonal shape of the facet. Bright (dark) spots in the middle of the $dI/dV$ maps correspond to a higher (lower) $dI/dV$ signal for the spectra taken at the center of the facet as compared to spectra averaged over the whole facet.

In Fig. 30 the complete data set consisting of 100 $dI/dV$ maps is displayed. The number of nodes and antinodes increases with increasing voltage and even for the largest voltages nodal patterns are observable.

In Fig. 31a we show another cluster with a height of $h = 2.5$ nm and a facet area of $\Omega = 47$ nm$^2$, which results in a cluster size of $N = 1 \times 10^4$ atoms. In the corresponding $dI/dV$ maps (Fig. 31b) again nodal patterns are visible, although the signal-to-noise ratio is lower compared to the maps of Fig. 29. As before, the energy positions of the maps correspond to maxima and minima in the center of the measured $dI/dV$ spectra for this cluster.

The $dI/dV$ maps on the two cluster facets remind of similar patterns which were measured for a two dimensional confinement of the surface state on a Ag(111) surface inside the hexagonal step edges of small 1 ML Ag islands grown on the surface [32,70]. For the silver islands the state with lowest energy $E_1 = -52$ meV without nodes inside the hexagon is close to the onset of the parabolic dispersion of the Ag(111) surface state at $E_0 = -67$ meV. In our data the lowest energy states with $E_{a1} = -455$ meV (Fig. 29) respective $E_{b1} = -530$ meV (Fig. 31) are close to the corresponding energy for the Au(111) surface which was measured to $E_0 = -487$ meV with UPS [71]. But we want to stress the main difference to previous experiments for metal on metal systems, e.g., in Ref. [70], where the

![Fig. 29. STS data measured on the (111) top facet of the cluster shown in Fig. 28. Top: $dI/dV$ spectra measured in the center of the facet (full dots) and averaged over the total facet area (open dots), respectively. The facet shape is shown in the inset (10 nm × 10 nm). Bottom: $(dI/dV)$ maps (4.5 nm × 4.5 nm) for five different voltages corresponding to the energy positions in Table 4. From Ref. [34].](image)
surface state exists in the Ag(111) surface, extending about 12 ML into the bulk [72], and the hexagonal 1 ML islands produce standing wave patterns due to scattering at the step edges [19,73,74]. In our experiments the Shockley surface state does not exist in the HOPG substrate but only within the clusters of about $10^4$ atoms. This points to an electronic structure of the clusters which is already very close to the bulk, including details like the occurrence of a gap in the surface projected band structure. Due to the small facets the level distance is increased compared to the Ag islands of Ref. [70] and thus most of the states are resolvable with STS without a significant mixing.

In Fig. 32 we show an averaged $dI/dV$ spectrum measured on the cluster of Fig. 29 with $N = 1.5 \times 10^4$ atoms for $V = -1.4, \ldots, +1.4$ V. Because measurements with $|V| > 0.5$ V induced the danger of tip changes, we measured only single $dI/dV$ spectra and no $dI/dV$ maps for this extended energy range. In addition to the peaks already visible in Fig. 29 one can observe a strong step like structure at about $-0.5$ eV which is typical for a two dimensional Shockley surface state, and its energy is close to the corresponding step for a Au(111) surface. Similar spectra were obtained for the cluster of Fig. 31 with $N = 1 \times 10^4$ atoms, but not on other, generally smaller clusters without such a pronounced nodal pattern on the facet [69].
We can describe the experimental data quantitatively using the model of Ref. [70], describing the two dimensional confinement of Shockley surface states, if we allow for a cluster size dependent energy shift of the surface state dispersion (cf. Table 4). The model of Ref. [70] gives

\[ E_{\text{calc}} = E_0 + \left( \frac{\lambda_n}{\Omega} \right) \cdot (m_e/m^*) \]

with the values of \( \lambda_n \) for a hexagonal confinement. For \( m^* \) we use the effective mass \( m^* = 0.26m_e \) of the Au(111) surface state as determined with ARUPS (see below). As the only free parameter we adjust the surface state onsets \( E_0' = -528 \text{ meV} \) and
We estimate the error of the experimental energies to ±15 meV. The accuracy of the theoretical values is determined by the error of ±5% for the facet area. Modes which could not be observed in STS are printed in italics.

\[ E_b = -588 \text{ meV} \]

for the two clusters of Fig. 33 so that the energies \( E_{1a,1b} \) are identical in experiment and theory, respectively. We obtain an excellent agreement for the energies corresponding to the peaks in the \( dI/dV \) spectra and for the measured \( dI/dV \) maps with the calculated state densities shown in Ref. [70]. In Table 4 the calculated and measured energy levels are summarized. The respective theoretical and experimental standing wave patterns are displayed in Fig. 33. The energy axis is scaled in such a way that the position of the energy levels is independent of the facet area \( \Omega \). The different modes are consecutively numbered with regard to their energies \( E_n \) with \( n \geq 1 \).

In addition the modes are compared to the eigenstates inside a 2D circular box of radius \( r \). The wavefunction is given by \( \psi_{m,l}(\rho,\phi) \propto J_1(l_{m,l}\rho)e^{il\phi} \) with the Bessel function \( J_1 \) and the wavenumber \( k_{m,l} = z_{m,l}/r \). With given radius \( r \) the \( m \)th zero crossing \( z_{m,l} \) of the \( l \)th order Bessel function defines the energy \( E_{m,l} = \hbar^2 k_{m,l}^2/(2m^* ) \) [75]. This gives \( E_{m,l} = E_0 + (\hbar^2\pi/2) \cdot z_{m,l}^2/(\Omega \cdot m^* ) \) for the energies of the different modes. As it can be seen in Fig. 33 the energy positions of the modes which were clearly observed in the experiment (cf. Figs. 29–31) correspond nicely to the modes with \( l = 0,1 \) and the corresponding calculated energy positions in the hexagonal confinement differ only by a small amount. Consequently the energy difference between the surface state onset and the lowest energy mode, scaled with the facet area, i.e., \( (E_1 - E_0) \cdot \Omega \) is also nearly identical for the hexagon confinement (2.725 eV nm\(^2\)) and the circular confinement (2.662 eV nm\(^2\)).

In order to fit the absolute energetic position of the first center antinode mode \( E_1 \), the minimum of the parabolic dispersion of the surface state at \( E_0 \) has to be shifted to lower energies compared to the onset of the surface state band on a macroscopic gold surface \( (E_0^{\text{bulk}} = -487 \text{ meV}) \) [71]. This can be related to the shift of the surface state to lower energy for thin metal films due to the interaction with the substrate within the decay length of the surface state [76] or with possible shifts due to film strain [77]. The minor influence of a field induced Stark shift [78,79] is neglected here. We use the two fix points for \( E_0(h) \) given above together with the limiting value \( E_0(\infty) = -487 \text{ meV} \) to set up a parameterization of \( E_0(h) \) as used in [76]. This results in the formula

\[ E_0(h) = -487 \text{ meV} - 491 \text{ meV} \cdot \exp(-h/1.581 \text{ nm}) \]  


<table>
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<th>( n )</th>
<th>( \lambda_n ) (eV nm(^2))</th>
<th>( E_{n,\text{calc}} ) (meV)</th>
<th>( E_{n} ) (meV)</th>
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Together with the model for the confinement of the two dimensional electron gas to a hexagonal box from Ref. [70] we can now calculate predicted energy positions for all different clusters. The cluster height determines the surface state onset, while the scaling for the peak positions is given by the facet area.

We were able to show, that this model quantitatively describes the STS spectra for clusters above about $10^4$ atoms cluster size [69]. Below this cluster size the agreement disappears, even if the clusters still show facets on top.

### 6.2. Photoelectron spectroscopy

With UPS it is not possible to address single clusters as with STS, but given the typical focal area of the analyzer ($10^7 \mu m^2$) and a cluster density of $\rho_c \approx 10^5 \mu m^{-2}$ we always average over about $10^{10}$ clusters for our samples. So different from scanning tunneling
experiments, where the size distribution allows gathering information about a broader range of cluster sizes and morphologies with a single sample preparation, in the case of UPS different cluster sizes lead to a loss of information, mainly due to inhomogeneous broadening.

The d-band spectra of large, faceted Au clusters (Fig. 11) are already very close to the bulk Au(111) spectra. This indicates that the bulk like treatment of these clusters is justified. Above a critical cluster size the d-band structure does not change anymore significantly, hence the size distribution does not lead to noticeable spectral broadening. Nevertheless, other influences on the UPS curves as, e.g., the dynamic final state effect (cf. Section 7) have to be considered, which also may include a size dependence. The Shockley surface state on the cluster facets should also be visible in UPS spectra near the Fermi edge.

Angular resolved spectra for the corresponding bulk system, a Au(111) film on mica (thickness \(\approx 10^2\) nm), with an angular resolution of \(\pm 1^\circ\) are shown in Fig. 34. In normal emission, i.e., at the \(\Gamma\) point of the surface Brillouin zone, the surface state peak is located about 430 meV below the Fermi level. With increasing emission angle it shifts towards higher energies until it crosses the Fermi level and becomes unoccupied. The parabolic shift reflects the free electron like nature of the surface state. We performed a detailed analysis, taking into account the finite angular and energetic resolution of our setup [80]. The fit of the model to the experimental data reveals the surface state onset \(E_0^{bulk} = (-445 \pm 5)\) meV and the effective mass \(m^*/m_e \approx 0.25\). ARUPS measurements of a Au(111) single crystal with extremely high resolution (\(\Delta E \approx 3.5\) meV FWHM; Data from Ref. [80].

Fig. 34. Angle resolved photoelectron spectra (dotted curves) of a Au(111) film (thickness \(\approx 10^2\) nm) grown on mica after background subtraction (see Ref. [80] for details). The emission angle is varied from about \(-5^\circ\) (bottom) to \(+6^\circ\) (top) in steps of \(1^\circ\). The curves are shifted vertically for clarity. The sample temperature was \(T = 50\) K and the photon energy \(h\omega = 21.2\) eV. The thin solid lines represent the fit for a parabolic dispersion including a model for the finite experimental angular and energetic resolution [80]. The agreement between experiment and calculation is nearly perfect. The calculated spectrum closest to normal emission is plotted with a thick line.
\( \sigma_x \approx 0.15^\circ \) result in \( E_{\text{bulk}}^0 = -487 \text{ meV} \) and \( m^*/m_e = 0.26 \) [71]. The discrepancy of the onset energies is probably caused by residual stress of the Au film of mica, forming \( \mu \text{m} \) sized crystallites with large cloughs in between [80]. More recently, a value of \( E_{\text{bulk}}^0 = (-479 \pm 2) \text{ meV} \) has been reported [81], which reduces the discrepancy to \( \approx 30 \text{ meV} \). The splitting of the surface state due to the spin–orbit interaction reported in Ref. [71] is only visible for angular resolutions significantly better than \( \pm 1^\circ \).

The spectra in Fig. 35 were measured for the cluster sample discussed in Section 6. They also show, on top of the Fermi level onset an extra peak at an energy of about \(-0.5 \text{ eV} \) for normal electron emission, i.e., \( k_\parallel = 0 \), which disappears for angles \( \pm 3^\circ \) off normal emission. In addition a significant broadening occurs, together with an asymmetric behavior with regard to the emission angle. These effects are discussed in more detail in Section 8. The peak position in normal emission is similar to the bulk Au(111) surface, except for a shift of about 0.1 eV to lower energies for the cluster sample.

The broad structure in the UPS spectra of Fig. 35 is supposed to be given by the average over the first confined state \( E_1 \) for different clusters. The disappearance of the peak structure for off-normal emission was interpreted as a remnant of the two dimensional dispersion for a surface state [34]. Similar effects occur at vicinal Ag(111) [82] and Au(111) [83] surfaces for the direction perpendicular to the steps. Due to the broad features and the weak dispersion of the cluster spectra the finite angular resolution of the analyzer does not result in a significant effect on the line shapes. For \( E_n \) with \( n > 1 \) corresponding peak structures are not visible in Fig. 35 due to the averaging over a broad range of facet sizes and cluster heights and the additional “dynamic final state effect” in the photoemission process. These influences are discussed in detail in Sections 7 and 8.

Fig. 35. Angle resolved photoelectron spectra of cluster sample D, measured at \( T = 50 \text{ K} \). The emission angle was increased in steps of \( 1^\circ \) from about \(-3^\circ \) to \( 3^\circ \). Instead of the continuous dispersion of the surface state (cf. Fig. 35), its peak intensity essentially gets broader and vanishes at higher emission angles. The shape of the Fermi edge is characteristic for Au clusters on graphite. It is discussed in detail in Chapter 7. From Ref. [34].
7. Dynamic final state effect

The photoemission data of supported metal clusters presented hitherto were discussed in view of the initial density of states. But in general also final state effects have to be taken into account. The final state in the case of free clusters is characterized by the excited photoelectron and the corresponding hole in the cluster (see Fig. 36a). The lifetime of the positive charge on the isolated cluster is large compared to other timescales of the experiment, allowing a description from a static point of view. If the clusters are coupled to a substrate, the situation is different and the dynamics of the photoemission process become important (Fig. 36b). In this section a simple model is discussed which allows to describe the influence of this “dynamic final state effect” on a quantitative level. In the earlier experimental investigations of this effect silver was used as a cluster material for which the photoemission spectra at the Fermi edge were easier to interpret than for gold clusters because of the absence of the surface state near the Fermi edge due to the more spherical morphology, showing no indication for flat top facets [28,29]. Nevertheless, the same effect will be used for the interpretation of angle resolved UPS on Au clusters, as shown in Section 8.

Already several years ago so-called “postcollision effects” were the subject of intense research. Originally investigated for collisions between atoms and ions [84], the interest shifted to core level photoemission experiments, where slow “threshold” electrons are influenced significantly by these effects because they are still close to the primary ionized atom on the timescale of the core hole decay, which is partly accompanied by an Auger electron emission (for a review see e.g., Ref. [85]). The closer the threshold electron is to the excited atom during its core hole decay, the larger is the energy loss for the threshold electron and the energy gain for the Auger electron. The statistical nature of the core hole decay leads to a distinct broadening of the corresponding threshold and Auger electron lines. Often, semiclassical theories are sufficient to reproduce the experimental data [86].

If molecules adsorbed on a surface are studied, the postcollision process gets modified by screening [87], which mainly reduces the total magnitude of the energetic shifts, leading to smaller broadening effects, i.e., to more narrow electron lines. In addition screening charge transfer effects can lead to double peak structures [88].

Fig. 36. Schematic illustration of the photoemission process from a metal cluster. (a) For a free cluster the photohole persists within the relevant electron–hole interaction time and the kinetic energy of the photoelectron is lowered according to Eq. (14). (b) Immediately after the photoexcitation in a supported cluster the electron–hole interaction is analogous to (a). At a certain time \( t \) the photohole may be screened or neutralized and the corresponding change of the interaction affects the kinetic energy of the electron. The smaller the distance \( vt \) is at the time \( t \), the larger the influence on the kinetic energy is.
For free, i.e., non-deposited molecules or clusters, the singly positive charge state due to photoelectron emission from valence states close to the Fermi energy by ultraviolet or X-ray photons remains constant over a time scale sufficient to let the photoelectron completely escape (cf. Fig. 36a). As a result, well defined, sharp spectral electron lines are obtained. Higher charge states which occur for multiple photoionization lead to the superposition of several photoelectron spectra with relative shifts given by the charging energy [89]. In the case of large metal clusters, the energy difference between two charge states can be calculated in good approximation by the classical value given by $e^2/4\pi\varepsilon_0 R$ with $R$ being the cluster radius. For the absolute energetic position with respect to the corresponding bulk material (defined by the limit $R \to \infty$) the size dependent change of the work function has to be considered in addition. For the difference between the ionization energy of a cluster and the work function of the corresponding bulk material this can be approximated by an additional factor $\alpha$ of the order of 1, depending mainly on the electron density of the metal [90].

For metal clusters on a substrate, the size dependent energetic shift is altered due to the additional interaction with the surface (cf. Fig. 36b). However, unlike the postcollision induced effects for threshold electrons described above, here they lead to an enhanced broadening of the spectral lines. This can be attributed to the statistical nature of the screening or charge transfer processes itself. The total energy is not shared by the photoelectron and an Auger-electron, but some fraction is transferred to the cluster/surface system. As a consequence, characteristic distortions of the spectral features close to the Fermi level occur. It turned out that a semiclassical model was sufficient to reproduce the dynamic final state effect in the experimental data [28,29]. Within the model, the elimination of the positive charge is described by a characteristic time $\tau$. The probability that the charge is eliminated during the time interval $[t, t + dt]$ is given by

$$P(t)\, dt = (1/\tau) \exp(-t/\tau) \, dt.$$  

(12)

In order to calculate the energy of the electron arriving at the electron analyzer, we need the potential $W(r)$ acting on the electron on its way from the cluster to infinity, with $r$ being the distance from the center of the cluster. A simple formula is given by

$$W(r) = W_{\text{max}} - \frac{ze^2}{4\pi\varepsilon_0} \frac{1}{r},$$  

(13)

which fits the limiting cases $W(R) = 0$ and $\lim_{r \to \infty} (W_{\text{max}} - W(r)) \propto 1/r$. If the influence of the positive charge vanishes at the time $t$, the total energy loss of the photoelectron compared to the case of a neutral cluster is $W(R + vt)$, where $v$ is the photoelectron velocity. Thus, the constant $W_{\text{max}}$ in Eq. (13) corresponds to the maximum energy shift for $t \to \infty$. In the case of a free cluster this shift is roughly the difference between its ionization potential and the work function of the bulk material [91]. A semiclassical density variational calculation for free silver clusters has shown that the shift follows the relation

$$W_{\text{free max}} = \frac{ze^2}{4\pi\varepsilon_0} \frac{1}{R},$$  

(14)

with $\alpha = 0.41$, in agreement with experimental results for small silver clusters [92]. For supported clusters, however, the actual maximum shift $W_{\text{max}}$ may differ from Eq. (14). Details of the cluster–surface coupling and of the individual cluster morphology are expected to induce deviations from the simple potential expression in Eq. (13), as well as from the
assumption of a universal characteristic time $\tau$ according to Eq. (12). In practice we will treat $W_{\text{max}}$ as a fit parameter and use Eq. (14) for a plausibility check of the result. The statistical nature of the time $t$ (cf. Eq. (12)) leads to a distribution of energy shifts, even if all clusters are identical in radius and coupling to the substrate. The time distribution (Eq. (12)) can be transformed into an energetic one:

$$P(W) dW = P(t(W)) \frac{dW}{dW(t)} dW, \quad W \in [0, W_{\text{max}}]. \tag{15}$$

Inserting $W(R + vt)$ one gets with $C = R/v\tau$

$$P(W) dW = \left(\frac{CW_{\text{max}}}{W_{\text{max}} - W}\right)^2 \exp\left(-\frac{CW}{W_{\text{max}} - W}\right) dW. \tag{16}$$

This function is plotted in Fig. 37a for several values of $C$, giving the magnitude of the cluster–substrate interaction. For $C \ll 1$ (i.e., $\tau \to \infty$) the distribution approaches a $\delta$ function located at $W = W_{\text{max}}$. For $C \gg 1$ (i.e., $\tau \to 0$) the photohole is immediately eliminated and $P(W)$ approaches a $\delta$ function centered at $W = 0$.

The expected experimental spectrum $d(E)$ can be calculated by a convolution of the intrinsic function $f(E)$ (which approaches the bulk spectrum for large clusters) with the distribution of energy shifts $P(W)$:

$$d(E) = P(E) \otimes f(E) = \int_{-\infty}^{+\infty} P(W) f(E - W) dW. \tag{17}$$

Resolution induced broadening effects are neglected here. The afore mentioned limiting case $C \ll 1$ results in a simple shift of the spectrum by $W_{\text{max}}$, whereas the effect vanishes for $C \gg 1$. In the intermediate region the shift is associated with a broadening of spectral features.

If we assume a radius dependency of $W_{\text{max}}$ according to Eq. (14) the cluster size distribution will affect the shape of $PW$:

$$P(W) = \int_0^{+\infty} g(W_{\text{max}}) \left(\frac{CW_{\text{max}}}{W_{\text{max}} - W}\right)^2 \exp\left(-\frac{CW}{W_{\text{max}} - W}\right) dW_{\text{max}}, \tag{18}$$

Fig. 37. Calculated distributions $P(W)$ for different coupling values $C$. The curves were calculated for (a) monodisperse clusters according to Eq. (16) and (b) for a size distribution of $R = \langle R \rangle \pm 0.2\langle R \rangle$ using Eq. (18). From Ref. [29].
with \( g(W_{\text{max}}) \) being the probability function of \( W_{\text{max}} \). The result for a Gaussian radius distribution with \( R = \langle R \rangle \pm 0.2 \langle R \rangle \) is plotted in Fig. 37b for the same values of \( C \) as for the monodisperse clusters. Interestingly, the size distribution does only provide a significant influence in the range \( C < 1 \). For broader size distributions of the width \( \sigma = \sigma_R/\langle R \rangle \geq 0.5 \) a log-normal distribution should be used instead of the Gaussian in order to avoid an unphysical step at \( R = 0 \).

The change of the Fermi-edge shapes induced by the dynamic final state effect is most clearly seen at low temperatures where the thermal broadening is negligible. These low temperature spectra, which were the topic of a previous study [28] are summarized here.

The shape of the Fermi edge can be approximated by a step function for low temperatures. The dynamic final state model predicts spectra as shown in Fig. 38 for several coupling values \( C = 10^{-3}, \ldots, 10^2 \). For uniform cluster sizes one gets the dashed curves and the consideration of a size distribution with \( R = \langle R \rangle \pm 0.2 \langle R \rangle \) results in the solid curves in Fig. 38. In the intermediate region \( C \approx 1 \) the dashed spectra are nearly identical to the solid ones. Whereas the upper edge is always rounded for inhomogeneous cluster samples, a characteristic sharp kink at the Fermi energy exists for both regimes.

The photoelectron spectrum for silver clusters with \( \langle h \rangle = (3.9 \pm 0.8) \text{ nm} \) (i.e., \( R = \langle R \rangle \pm 0.2 \langle R \rangle \)), measured at \( T = 40 \text{ K} \) (see Fig. 39, top) could be described by the model by choosing \( C = 3.0 \) and \( W_{\text{max}} = 0.49 \text{ eV} \). According to Eq. (14) the latter value deviates significantly from the charge energy \( W_{\text{free max}} = 0.23 \text{ eV} \) of a free silver particle with \( R = 2.5 \text{ nm} \), which is the radius of a sphere with the same volume as the average cluster size within the truncated sphere model (cf. Eq. (3)). But this is not unexpected as discussed above. The fit value of \( C \) corresponds to \( \tau = 0.3 \times 10^{-15} \text{ s} \), pointing to an electron dynamics on the femtosecond timescale. Because of the simplifications in the semiclassical model \( \tau \) should not be taken too seriously as a quantitative measure for the timescale of the cluster substrate interaction. But nevertheless by choosing the best parameters \( C \) and \( W_{\text{max}} \) one can use \( P(W) \) to model the dynamic final state effect very well.

Fig. 38. Expected shapes of the Fermi edge within the dynamic final state model. The abscissa is rescaled in order to drop the dependence on \( W_{\text{max}} \) and the intensity is normalized to 1. For monodisperse clusters the two limiting cases \( C \ll 1 \) and \( C \gg 1 \) result in sharp edges (dashed lines), whereas a finite size distribution (here \( R = \langle R \rangle \pm 0.2 \langle R \rangle \)) results in a broadening, in particular for \( C \ll 1 \) due to the corresponding distribution of \( W_{\text{max}} \) (solid lines). From Ref. [28].
Further support of the model assumptions results from the variation of temperature and photon energy. At room temperature the characteristic kink at the Fermi level vanishes and the spectrum seems to be very similar to a shifted Fermi edge (Fig. 39, bottom). This shows that the measurements at low temperatures are advantageous for the investigation of the dynamic final state effect. Utilizing sophisticated deconvolution techniques \[93,94\] it is possible to extract \( P(W) \) as we will use it in the next section.

The influence of the electron velocity can be investigated even at room temperature, in spite of the thermal broadening, if the photon energy is varied over orders of magnitude. This concept was successfully tested and discussed in Ref. \[95\].

8. Intercomparison of STS and UPS for large clusters

The use of the two complementary methods UPS and STS permits experimental access to both, the momentum dependent and the spatially dependent density of states. In this section the interconnection of the measurements will be discussed considering as example large gold clusters on HOPG. The focus is on the influence of the surface state confinement within the cluster facets on the experimental STS and UPS spectra. In particular it is explained how the discrete levels have to be translated into the rather broad UPS features.

In the case of gold clusters on graphite the energetic gaps between the discrete surface state levels are larger than 0.1 eV. Hence the discrete electronic structure should be resolvable with our UPS apparatus. However, the cluster size distribution and the dynamic final state effect result in an additional broadening of the features. In this section these contributions are analyzed in detail which allows a self-contained and complete view of the confined surface state on the top facets of large gold clusters on graphite.

8.1. Angle resolved photoemission

In order to investigate the effect of the surface state on the facets of large gold clusters we prepared a sample optimized for the low temperature photoemission experiment. The
Au evaporation was done in a single step and the UPS measurement was subsequently carried out without STM investigations in between. Since the surface state is very sensitive to contamination, special care was taken to assure clean UHV conditions. The gold evaporation was performed at \( T = 350 \, ^\circ\text{C} \) and the subsequent UPS measurements were done at \( T = 50 \, \text{K} \). The temperature was not set below 50 K in order to avoid the increasing contamination rate of the sample surface at lower temperatures. The Au exposure for this new sample F was about \( \Gamma_{\text{evap}} = 1.0 \, \text{ML} \) which is comparable to samples C and D.

Angle resolved photoelectron spectra with an angular resolution of about \( \sigma_\theta \approx 1^\circ \) were taken for the energy region near the Fermi level. In Fig. 40a the raw data are plotted for different emission angles with respect to the surface normal vector. The angle between the helium lamp and the normal emission direction of the analyzer is 45°. The emission angles in Fig. 40a range from \( \Theta = -7^\circ \) (towards the He lamp) to \( \Theta = +5^\circ \) (in the opposite direction). The uncertainty of the absolute angular scale is about \( \pm 1^\circ \) given by the accuracy of the sample alignment. The relative angles, i.e., the angular distances between two spectra is exact within \( \pm 0.2^\circ \). The spectra exhibit two main features: First, at normal emission a peak arises at \( E \approx -530 \, \text{meV} \) similar to the spectra of Fig. 35. This peak shows an asymmetric broadening and an intensity decrease with varying emission angle. The second feature is the Fermi edge, which is distorted and shifted towards lower energies compared to the bulk Fermi edge. The shape change can be related to the final-state interactions during the photoemission process discussed in Section 7. Within the dynamic final state effect the spectra \( d(E) \) result from a convolution of the intrinsic (potentially \( k_\parallel \) resolved) density

![Fig. 40. Angle resolved UPS data of sample F \( (T = 50 \, \text{K}, \hbar\omega = 21.2 \, \text{eV}) \). The emission angles with respect to the surface normal are given next to the respective curves. The spectra are shifted vertically for clarity. (a) The raw data show the peak caused by the surface state (cf. Fig. 35). (b) Spectra after subtraction of the data at \( \Theta = +5^\circ \).](image-url)
of states \( f(E) \) with a function \( P(W) \) representing a probability distribution of energetic shifts. In addition broadening effects like the finite analyzer resolution have to be taken into account, which are combined in the instrument function \( u(E) \). All entire broadening and shifting effects can be summarized by a blurring function \( g(E) \):

\[
d(E) = (P \otimes u) \otimes f \equiv g \otimes f
\]

\[
d(E) = \int_{-\infty}^{+\infty} \left( \int_{-\infty}^{+\infty} P(W)u(E' - W)\,dW \right) f(E - E')\,dE',
\]

where \( \otimes \) denotes the convolution. The convolution is applied on both, the background intensity with the Fermi edge induced by bulk Au sp-electrons, and the signal from the surface state on the cluster facets. Hence the functions \( f(E) \) and \( d(E) \) consist of contributions from the bulk (3D) and the surface (2D) electronic structure:

\[
d(E) = d_{2D}(E) + d_{3D}(E) \quad \text{and} \quad f(E) = f_{2D}(E) + f_{3D}(E).
\]

In order to extract the surface state contribution, which will be the focus of this section, we subtract from each spectrum the data at \( \Theta = +5^\circ \), where no remaining surface state signal is detectable. The resulting surface state intensities \( d_{2D}(E) \) are plotted in Fig. 40b, and they form the basis of the further discussion.

In the background subtracted data the asymmetry mentioned already in Section 6 is even more striking: Whereas for positive angles (i.e., in the direction off the He lamp) the intensity essentially disappears quickly without a noticeable dispersion, in the other direction towards the lamp the main contribution to the overall intensity shifts to higher energies with slowly decreasing signal, vanishing at angles \( \Theta < -7^\circ \). The only asymmetry of the experimental setup with respect to the emission angle is given by the incident angle of the photons: for negative values of \( \Theta \) the incident angle approaches the surface normal direction. This points to an influence of either the photon wave vector parallel to the surface or the polarization of the light. Since the photon wave vector is only about 0.01 Å\(^{-1}\), the photon momentum appears to be negligible and the polarization effect should be taken into account. Similar effects have been observed in photoelectron spectra of the Cu(111) surface using p-polarized light [96], and they have been attributed to a varying momentum matrix element depending on the incident angle. However, considering the small incident angle variation of \( \approx 10^\circ \) here, the relative effect in our case is much larger than in Ref. [96] though we do not use polarized photons. The detailed origin of the asymmetry effect has to be investigated by varying the incident angle but this is not provided by our apparatus. Another possibility may be the use a different photon energy (e.g., ArI radiation) which changes the momentum \( k_f \) at the same emission angle. This could give hints about the origin of the effect and will be the topic of future experiments. However for the following discussion the asymmetric intensity of the spectra is not crucial.

We now turn to the analysis of the surface state peak shapes in Fig. 40b. The key question is how the observed spectra fit to the expected DOS for the confined surface states of an ensemble of faceted Au clusters. The effects leading to a peak broadening are of special interest, which are the finite angular and energetic resolution of the analyzer, the dynamic final state effect and the inhomogeneous cluster ensemble, i.e., the influence of a distribution of cluster heights and facet areas. As already mentioned in Section 6 the finite angular resolution is negligible here because of the weak dispersion and the broad structures. We thus concentrate on the latter two effects.
Whereas the first peak, originating from the $n = 1$ mode in the hexagonal “particle-in-a-box” model (cf. Section 6), is clearly visible in normal emission, already the second peak can only be identified as a shoulder in the tail of the first one. A main contribution to the spectral broadening is induced by the function $g(E)$ in Eq. (19). The inversion of the convolution, i.e., the deconvolution of the data, should allow to extract the intrinsic electronic structure of the cluster sample. The only remaining effect would be the inhomogeneous broadening. The deconvolution is done with the ‘adaptive kernel maximum entropy method (AK-MEM)’ described in [48,93,94,97]. This powerful technique widely overcomes the well-known artifacts of other maximum-entropy based deconvolution methods such as ringing phenomena or the generation of similar artificial structures. Moreover, it does not require any external parameters and thus provides an impartial output including statistically determined confidence intervals. Necessary inputs are the experimental spectrum $d(E)$, its error $\sigma_d(E)$, and the convolution function $g(E)$. The question now is: what is the correct $g(E)$ which describes the deviation of the data from the intrinsic electronic structure of the cluster ensemble? The idea is to extract $g(E)$ from data which are not influenced by the Shockley surface state and where the intrinsic structure is well known. In other words, the linear nature of the convolution allows to extract $g(E)$ from the 3D part of the spectra and then apply it on the 2D contribution by a deconvolution. For this purpose we choose the ARUPS spectrum at $\Theta = +5^\circ$, containing no noticeable contribution of the surface state, i.e., we assume $d_{2D}(E) = f_{2D}(E) = 0$ for this angle. The spectra shown in Fig. 40a still contain the graphite signal. This background was measured before the metal evaporation with identical analyzer and photon source parameters and is now subtracted because the dynamic final state effect, which is included in $g(E)$, does not necessarily have an effect on the HOPG spectrum. In addition a small linear background is subtracted in order to set the intensity above the Fermi level (probably induced by satellites in the HeI radiation) to zero. The processed spectrum $d_{3D}(E)$ is shown in Fig. 41 (dotted curve).

![Graph showing background corrected UPS spectrum at $\theta = +5^\circ$](image)

Fig. 41. Background corrected UPS spectrum at $\theta = +5^\circ$ (dots) and the intrinsic model function (solid line) consisting of a straight line multiplied by a step function.
For large, faceted Au clusters the electronic structure is already close to the bulk limit. Hence, for the intrinsic function $f_{3D}(E)$ we assume a step function multiplied by a straight line. Since the sample temperature was $T \approx 50$ K, the thermal broadening of the Fermi function ($kT \approx 2.8$ meV) can be neglected compared to the smooth behavior of the measured curve (cf. Fig. 41). The straight line represents the first order fit to the density of states below the Fermi level and it fits the low energy part of the UPS result very well (see Fig. 41, solid line). The two curves of Fig. 41 are related via a convolution with the required $g(E)$:

$$d_{3D}(E) = g(E) \otimes f_{3D}(E). \quad (21)$$

By applying a deconvolution of the two step-like functions we are now able to extract $g(E)$. For this purpose a method different from the mentioned AK-MEM is applicable because of the simple form of the intrinsic function $f_{3D}(E)$. The key idea is to transfer the deconvolution with a step function, which is essentially the derivative of the original data, to the function $f_{3D}(E)$ which is extended by a straight line. Subsequent to the deconvolution the experimental spectrum is smoothed using the AK-MEM technique in order to reduce the noise. The resulting blurring function $g(E)$ as shown in Fig. 42 exhibits a clear asymmetry with a tail towards negative energies, and it was tested by the convolution of the sharp step function with $g(E)$ which fits perfectly the measured UPS data. The effect on the UPS data besides the broadening is a shift to lower energies in the order of some 10 meV. Therefore the subsequent deconvolution is not only expected to sharpen the spectral features, but it also corrects the energetic positions. Above the Fermi edge a few wiggles are visible due to the low signal-to-noise ratio of the underlying data in this region and due to numerical reasons behind the sharp edge of the peak ("ringing" effects). But the amplitude of these oscillations is negligible compared to the main peak and the effect on the deconvoluted UPS spectra will be marginal.

The next step is to deconvolute the experimental data of Fig. 40b with $g(E)$, yielding $f_{2D}(E)$. The complete procedure is analogous to the determination of an apparatus function from experimental data (e.g., the elastic line in a scattering experiment) and then using it for the deconvolution of the spectra [94]. In Fig. 43 the maximum posterior (MAP)

![Fig. 42. Deconvolution result of the two functions of Fig. 42. The plot represents the smoothed result (see text).](image-url)
result (cf. Ref. [48,93]) for the normal emission spectrum ($\Theta = 0^\circ$) is shown. The displayed confidence region is the pointwise standard deviation of the posterior probability cloud in

![Fig. 43](image)

Fig. 43. Maximum posterior (MAP) result (thick line) of the AK-MEM deconvolution of the normal emission spectrum (dots, cf. Fig. 40b). The hatched area represents the confidence interval around the reconstruction $f_{2D}(E)$. The thin line through the data points is the deconvoluted MAP function, convoluted again with $g(E)$ (see Fig. 42). It should fit the data points and therefore serves as an additional check for the reliability of the MAP result.

![Fig. 44](image)

Fig. 44. MAP results $f_{2D}(E)$ for the deconvolution of all angle resolved UPS spectra of Fig. 44b. Note the completely different behavior of the angular dependence compared to the bulk Au(111) surface state (Fig. 34).
Gaussian approximation. It gives a rough estimate of the reliability of the reconstruction \( f_{2D}(E) \), but it often overestimates the actual uncertainty.

Clearly observable is the energetic upward shift of the first peak by about 40 meV, located now at \( E_1 \approx -490 \text{ meV} \), and the emergence of a second peak at about \( E_2 \approx -260 \text{ meV} \). The little shoulder near the Fermi level is completely covered by the confidence interval and can not be taken seriously at this point. The asymmetry of the first peak is significantly reduced after the deconvolution which is most obvious at its low energy tail.

The deconvolution procedure can be applied on all angle resolved spectra using the same \( g(E) \). The results for the angle range \( -7^\circ \leq \Theta \leq 4^\circ \) are summarized in Fig. 44. Three peaks are distinguishable, reaching their maximum intensity at different emission angles.

From the STS analysis of confined surface states on the cluster facets (see Section 6) we expect that the peaks in \( f_{2D}(E) \) correspond to discrete modes within the hexagonal “particle-in-a-box” model. With regard to Eq. (10) the energetic distance between the first two peaks would roughly fit to facet areas around \( \Omega \approx 20 \text{ nm}^2 \), if we assign them to the \( n = 1 \) and \( n = 2 \) state, respectively. More detailed information about the cluster geometry is provided by STM measurements and this is used in the following for a quantitative simulation of the UPS spectra.

To get the DOS approximately from the spectra in Fig. 44, we can either sum up all angle resolved curves, or just select a single spectrum around \( \Theta = 2^\circ \). The latter case is justified because the mosaic spread of the substrate and an observed tilt of a few degree of some cluster facets but also the finite size of the facets itself lead to an uncertainty in \( k \) which is large enough to cover nearly the complete relevant angular region in one specific

![Fig. 45. Comparison of the ARUPS spectrum at \( \Theta = 2^\circ \) (lower curve) with the average over all angle resolved spectra (upper curve), both after the deconvolution of the dynamic final state effect. The residual peak shift is probably an artifact of the deconvolution since the peak amplitudes approach the size of the confidence interval for \( \Theta = 2^\circ \).](image-url)
direction of the dispersion. Consequently, both procedures yield very similar curves as can be seen in Fig. 45.

In summary we have seen that the angle resolved photoelectron spectra are not only influenced by cluster size or facet angle distributions. Main contributions, i.e., a blurring and a shift of spectral features, originate also from fundamental properties of the cluster–surface interaction and its effect on the photoemission process for small particles. However, the information about the quantization of the surface state is not lost. Utilizing state-of-the-art deconvolution techniques, it was possible to resolve the discrete levels. In the following the DOS averaged over a large number of clusters is simulated using STM and STS information in order to compare the two different methods UPS and STS on a quantitative level.

8.2. Cluster morphology

After finishing the photoelectron spectroscopy, the sample has been transferred into the STM. The images (see Fig. 46a) again reveal flat, nearly hexagonal facets similar to samples C and D. A few single adsorbates on the cluster facets are visible, probably due to the prior UPS experiment. Some of the clusters are located at large pits with a depth of more than one monolayer which results in an inaccurate height determination. Since in this section the absolute height will play an important role for the comparison of STS and UPS results, we do not include these clusters in the further discussion. Nevertheless, due to the similar effective capture radius as for the clusters grown in small pits or step edges, the size is not expected to differ significantly (cf. Section 4). The measured heights and facet areas of 68 clusters are summarized in Fig. 46b.

From the height distribution in Fig. 47 we deduce the mean cluster height $\langle h \rangle = 2.5 \text{ nm}$ with a standard deviation of $\sigma_h = 0.5 \text{ nm}$. The black line represents a fit of a log–normal distribution

![Fig. 46. (a) STM image (150 nm × 150 nm) of sample F. The two large pits in the upper and in the right region are two monolayers deep. (b) Measured cluster heights and facet diameters for 68 Au clusters. The straight line is taken from Fig. 13 and gives a lower limit for the observed cluster heights in dependence on the facet diameter. The crosses indicate clusters grown in pits with a depth of more than 1 ML, therefore their height, measured with respect to the upper plane of the HOPG surface, is underestimated.](image-url)
which is used here instead of a Gaussian in order to avoid an unphysical step at $h = 0$ for broad distributions. The gap voltage for the height determination was set to $V/NK = 2.5$ V for all topographic STM images which leads to a slightly underestimated height (cf. Section 2). Since for the determination of the parameters in Eq. (11) a similar voltage was used, this systematic error essentially cancels out.

The measured areas of the (111) top facets for the clusters of sample F are plotted in Fig. 47 b.

8.3. Simulation of UPS data

Knowing the morphology of each cluster, it is now possible to calculate the electronic structure of the confined Shockley surface state on the top facets using Eqs. (10) and (11). With this we get a level spectrum for each cluster, and by summing them up it should in principle be possible to simulate the expected angle integrated UPS spectrum. The calculated energy levels for sample F are shown in Fig. 48. Difficulties arise due to the low number of measured cluster heights and facet areas: calculating the density of states (e.g., by convolution with a Lorentzian), the statistical level bunching induces artificial features which are undistinguishable from true peaks arising by averaging over several $10^9$ clusters like in the UPS experiment. For this reason we assume log-normal distributions for both, the height distribution as well as the facet areas. For the simulation the two quantities are treated independently since no significant correlation is identifiable in Fig. 46b. Hence the total probability density function $P(h, \Omega)$ may be written as a product of the distributions for $h$ and $\Omega$.

From the measured cluster height distribution we use the parameters deduced from the log-normal fit in Fig. 47a. Though the number of counts is rather low, and therefore the deduced values are not very exact, we do not expect a significant influence on the calculated DOS. The different cluster heights result essentially in a constant broadening of
the spectra via the onset energies $E_0$, and the mean height determines an overall shift. In contrast the facet areas $\Omega$ sensitively affect the peak positions: a change of 5 nm$^2$ (compare Fig. 47) results in a shift of more than 100 meV for levels near the Fermi energy, which is already of the order of expected level distances. Therefore especially the width of the distribution decides whether discrete peaks are still observable in the simulated DOS. As a starting point we choose a log–normal distribution equivalent to Eq. (22) for $\Omega$ with an average value of $\langle \Omega \rangle = 19.5$ nm$^2$ as determined from the measured facet areas, and treat the width $\sigma_\Omega$ as a free fit parameter. The log–normal distribution with the best fit value $\hat{\sigma}_\Omega$ can then be compared with the measured distribution in Fig. 47b.

The simulation is performed by generating a sample of $m$ pairs of log–normal distributed random numbers, representing $m$ different clusters with height $h_1$ and facet area $\Omega_1$. Typically $m = 10^5$ clusters are generated, which is enough to avoid visible statistical noise. For each cluster $i$ the first five energy levels $E_{i,n}$ are determined using Eqs. (10) and (11). The line shape of an individual energy level $E_{i,n}$ is assumed to be Lorentzian, thus the DOS is calculated using

$$D(E) \propto \sum_{i=1}^{m} \sum_{n} a_{i,n} \Gamma_{i,n} \left( \frac{E - E_{i,n}}{2} \right)^{-1}, \quad n = 1, 2, 4, 7,$$

where $a_{i,n}$ is a weighting factor. In a first step only levels which could be observed by STS (i.e., high symmetry modes, cf. Section 6) are considered. Modes with $n > 7$ are neglected since their energetic positions are far beyond the Fermi level making them inaccessible for UPS. For the level width we use a constant value of $\Gamma_{i,n} = 20$ meV. It should be emphasized that this width does not necessarily correspond to the inverse lifetime. It is chosen in order to smooth the gaps between the Monte Carlo generated levels, and it roughly gives a lower limit to the minimum peak width in the STS curves. For hexagonal Ag adatom islands on Ag(111) an energy dependent width $\Gamma_{i,n} = 0.2(E_{i,n} - E_{i,0})$ has been found in the $dI/dV$ spectra [32]. From our STS results of faceted Au clusters on HOPG such a behavior is not evident (cf. Fig. 29). However, the final peak width of the simulated DOS will be essentially determined by $\sigma_\Omega$, rather than by $\Gamma_{i,n}$. In addition, also the choice

![Fig. 48. Calculated energy levels with $n = 1, 2, 4, 7$ (short lines to long lines) for the measured clusters in Fig. 46b. Note the statistically induced level bunching and vacancies for certain energy ranges.](image-url)
of the weighting factors is not crucial for the result. Here we assume that the photoemission probability from a specific cluster \( i \) is proportional to its facet area, i.e., \( a_{i,n} \propto \Omega_i \). We do not include an additional dependence on the quantum number \( n \). This is justified by the fact that for the levels below the Fermi energy the STS curves do not show a clear trend in the peak intensities. But also other models like \( a_{i,n} = \text{const} \) hardly change the shape of the resulting spectrum.

Fig. 49 illustrates the strong influence of the width \( \sigma_{\Omega} \) for the facet area distribution on the calculated curves. In order to allow for a better comparison with the experiment, the DOS curves are multiplied by a Fermi–Dirac function for the sample temperature \( T = 50\ \text{K} \). The comparison with the deconvoluted and averaged UPS spectrum in Fig. 45 suggests \( \sigma_{\Omega} \approx 0.25 \cdot \langle \Omega \rangle \), if one focuses on the first two peaks. However, none of the curves in Fig. 49 reproduces the third peak near the Fermi edge. Only for \( \sigma_{\Omega} \lesssim 0.15 \cdot \langle \Omega \rangle \) a weak maximum becomes visible at the Fermi cutoff, but such a narrow distribution is in contradiction to the histogram in Fig. 47. The discrepancy can be resolved by additionally including the \( n = 3 \) state in the sum of Eq. (23), which is located near the Fermi level for typical cluster sizes. At first glance this state is not identifiable in the STS curves, but we will come to this topic below. Fig. 50 shows the direct comparison of the calculated spectrum using \( \sigma_{\Omega} = 0.25 \cdot \langle \Omega \rangle \) and the levels \( n = 1, 2, 3, 4, 7 \) with the angle integrated UPS spectrum and the angle resolved spectrum for \( \Theta = -2^\circ \), respectively. We further on neglect the modes \( n = 5, 6 \) because no structures at the corresponding voltages are observable in the \( dI/dV \) curves (cf. Section 6) and even if they exist, the occurrence below the Fermi level is unlikely due to the exponential behavior in the tails of the probability distributions for \( h \) and \( \Omega \). The \( n = 7 \) mode is included because of its clear signature in the STS spectra (cf. Fig. 29),

![Fig. 49. Simulation results after multiplication with a Fermi function for three different distribution widths \( \sigma_{\Omega} \). For sharp distributions prominent peaks occur, whereas for larger \( \sigma_{\Omega} \) the structures disappear. Energy levels taken into account: \( n = 1, 2, 4, 7 \). The curves are shifted vertically for clarity.](image-url)
although this mode does not play any role for the simulated spectrum in this case, in order to be more flexible for other samples with larger facet areas.

The experimentally observed spectral features and their energetic positions are well reproduced by the simulation. The peak shapes show some deviations, but there exist explanations from the theoretical, as well as from the experimental point of view. First of all the photoelectron count rate is too low to specify the exact shape. This can be seen by the confidence intervals of the deconvoluted spectra (cf. Fig. 43). At least one order of magnitude better statistics would be needed for more detailed information. Secondly the model resulting into Eq. (23) is quite simple and experimental evidence which allow to specify the parameters affecting the peak shapes (like, e.g., $a_{i,n}$ and $\Gamma_{i,n}$) is missing so far. Even the facet area distribution is hard to determine experimentally due to the laborious quantification procedure of a large number of facet areas from the STM images.

As pointed out above, the log-normal distribution of the facet areas used for the simulation with $\sigma_\Omega = 0.25 \cdot \langle \Omega \rangle$ can now be compared a posteriori with the experimental histogram, which is done in Fig. 51a. Though the measured areas seem to be spread over a broader range, we would like to stress that the overall width is essentially determined by the largest measured facets. Taking into account the $\sqrt{N}$ uncertainty the applied width of $\sigma_\Omega = 0.25 \cdot \langle \Omega \rangle$ is not implausible within the statistical limits. In Fig. 51b a set of $m = 10^4$ randomly distributed heights and facet areas as generated by the simulation algorithm is shown in comparison with the measured values. Also in this plot the experimental points are covered by the Monte Carlo sample quite well which justifies the chosen value for $\sigma_\Omega$ a posteriori.
As discussed above, the simulations and the comparison with the UPS curves hint to the existence of a contribution from the \( n = 3 \) mode within the model of a free particle in a hexagonal box. This state could not be identified in the STS maps (cf. Fig. 30) so far. A possible explanation would be that the \( n = 3 \) signal is overwhelmed by the intensity arising from the \( n = 4 \) peak because of the low energetic distance (cf. Table 4) and the low DOS of the \( n = 3 \) mode near the facet center (cf. inset in Fig. 52). To check this we eliminate the \( dI/dV \) signal from the center region of the facet by subtracting a fraction of the center spectrum from the averaged spectrum (see Fig. 29):

\[
(dI/dV)_{\text{outer}} \propto (dI/dV)_{\text{average}} - a \cdot (dI/dV)_{\text{center}}.
\]  

(24)
The weighting factor $a$ is varied until the first peak completely vanishes, here $a = 0.35$. Since the $n = 4$ state also exhibits an intensity maximum in the center, this procedure should stress the outer regions. As shown in Fig. 52 the difference $(dI/dV)_{\text{outer}}$ is still nearly identical to the average curve, except for the fist peak and the peak around $V \approx -0.2$ V. Whereas in the averaged spectrum the latter peak exhibits an asymmetry, it now has a symmetric shape and is shifted to a lower energy position, which roughly corresponds to the $n = 3$ state. We note here that the dip at $V = 0$ V, i.e., the Fermi energy, occurs for all clusters independently of their height and facet area. Probably it is connected to the charge transport in the tip/cluster/surface system (cf. Section 5), perhaps in combination with the specific electronic structure of the HOPG surface [98].

The spatial symmetry of the mode can be checked by subtracting $dI/dV$ maps at the voltages corresponding to the $n = 3,4$ states from each other. Again a weighting factor is included in order to eliminate the intensity in the center. The result is added in the inset of Fig. 52 together with the theoretically expected symmetry as presented in Ref. [70]. Consistently, in both cases an enhanced intensity is visible at the corners of the facet. In summary, this analysis allows to draw the conclusion that the $n = 3$ level of the confined surface state probably contributes to the experimental photoelectron spectra.

9. Conclusions

We presented an experimental study for the geometric and electronic properties of gold clusters on graphite in a broad size range from a few ten to more than $10^4$ atoms per cluster. By using preformed nanopits in the graphite surface we were able to produce clusters
of different average size with a narrow size distribution. The size dependent morphology was characterized in detail with STM and TEM. In addition UPS was used to study the growth process.

The electronic properties of the clusters were investigated with STS and UPS. For clusters of a few ten up to about $10^4$ atoms per cluster a quantized electronic structure was only detected for individual clusters with STS. We could show that the observed peak structures in the $dI/dV$ curves are reproducible for individual clusters and show a systematic variation with the cluster size. While most of the structures in the STS data seem to be given by the cluster–surface system, some features are sensitive to the condition of the STM tip. Different possible mechanisms contributing to the STS spectra were discussed qualitatively or semi-quantitatively but a detailed quantitative interpretation was not yet possible.

For the specific case of the confined Shockley surface state on the top (111) facets of large gold clusters with more than $10^4$ atoms per cluster we were able to detect the quantized electronic structure with both techniques, STS and UPS. In this case a quantitative calculation of the energy levels for each individual cluster with given cluster height and facet area was possible. Using the cluster size distribution as measured with STM we achieved a quantitative agreement between the measured UPS spectra and the density of states obtained by averaging over the cluster size-distribution. Very important for the quantitative agreement was, however, the preceding deconvolution of the dynamic final state effect, which leads to a systematic asymmetric broadening of all spectral features.

We expect that the presented results will be important for the ongoing and future studies of clusters on surfaces, not only because they highlight some general features for the electronic properties of the cluster–surface system for clusters of different size, but also because they can demonstrate the consistent combination of STS and photoemission for the study of clusters on surfaces. Apart from the specific restrictions of both techniques the application to clusters on surfaces leads to additional phenomena which have to be included in the analysis of the experimental data.

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