Tunneling spectroscopy on silver clusters at $T = 5$ K: size dependence and spatial energy shifts

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Abstract

We have studied silver clusters grown in nanopits on a graphite surface using low-temperature scanning tunneling spectroscopy (STS) at $T = 5$ K. The pronounced peak structure measured in the STS data of the clusters is interpreted to have its origin in the quantized electronic structure of the cluster–surface system. Additionally, a systematic spatial energy shift was observed for some spectral features in $dl/dV$ maps on top of the clusters. © 2000 Elsevier Science B.V. All rights reserved.

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The investigation of the electronic structure of clusters and the question of how it is changed by the interaction with a surface is not only of fundamental interest, but also has several important applications, for example in the fields of future nanoelectronics or in catalysis [1–4].

We have developed a method for controlled cluster condensation on a nanostructured graphite surface [5], which enables us to produce metal clusters with a rather narrow size distribution in ultrahigh vacuum (UHV). High-resolution photoemission studies showed a cluster–surface interaction on a femtosecond timescale, which influences all spectral features, e.g. the spectra at the Fermi level onset [6] and the d-band structures [7]. In this paper we present scanning tunneling spectroscopy (STS) measurements for silver clusters grown on a nanostructured graphite surface. It is a natural idea to combine the benefits of photoelectron and scanning tunneling spectroscopy, because STS is able to probe the electronic structure of individual clusters. Even if one is able to deposit mass selected clusters on a surface [2,8,9], which is a very difficult and large-scale experiment, the clusters may have different isomers and orientations on the surface, and photoelectron spectra of the deposited clusters show averaged data, measured over a macroscopic area. On the other hand, the combination of photoelectron spectroscopy and STS may help in the difficult interpretation of the STS data, in which effects like the influence of the electronic structure of the tip, Coulomb charging of the cluster [10–12], the high electrical field within the tunneling region [13], and many more have to be considered. The
influence of some of these effects was already observed in tunneling experiments for clusters on surfaces, see e.g. Refs. [8,14–16]. However, the extraction of the electronic structure of the clusters from STS data is still an open question in current research.

The experiments were carried out in the surface science facility described elsewhere [17]. It combines scanning tunneling microscopy (STM) at \( T \leq 5 \) K and high-resolution (\( AE=10 \) meV) ultraviolet photoelectron spectroscopy (UPS) at \( T \leq 50 \) K. The clusters were produced by controlled condensation of silver evaporated onto a graphite (HOPG) surface with preformed pits of one monolayer depth and a diameter of \( 9 \pm 2 \) nm [5]. Before the silver evaporation was performed in UHV, the nanostructured HOPG surface was heated for \( 1 \) h at 870 K, and its cleanliness was checked by UPS. The size distribution of the clusters was determined by the combination of in situ UHV-STM for the height and ex situ transmission electron microscopy (TEM) for the lateral diameter [5]. A diameter-to-height ratio \( d/h = 1.4 \) was measured by comparison of TEM and STM data for several samples in the range \( h = 1.8–6.7 \) nm for the mean cluster height. The distribution of cluster heights for the sample used here was \( h = 1.4 \pm 0.3 \) nm.

Besides this direct determination of the cluster shape, we also calculated the total cluster volume and compared this with the amount of evaporated silver measured by calibration of the evaporation source with a quartz microbalance and additionally by STM images of silver grown as small islands with monoatomic height on an Ag(111) surface at \( T=250 \) K. From this comparison we get a sticking coefficient of about 0.5 for silver evaporated on the nanostructured HOPG at \( T=300 \) K, which is in agreement with measured sticking coefficients for copper and gold [18] if we consider the density of condensation centers given by the nanoparticles. In summary, we estimate that we can calculate the cluster volume with the height measured by STM using \( d/h = 1.4 \) with a relative accuracy of 30%. We checked that, within \( \pm 0.02 \) nm, the cluster height is independent of the tunneling voltage in the range \( 0.5–2 \) V.

The STM and STS measurements were performed at \( T=5 \) K. In overview images of 150 \( \times \) 150 nm\(^2\) we localized the clusters and then zoomed onto them in images of about 20 \( \times \) 20 nm\(^2\), where we measured tunneling spectroscopy data on typically five positions placed close to the very top of the clusters in the topological image, or took data on a grid of 10 \( \times \) 10 points, 1.5 \( \times \) 1.5 nm\(^2\) in size centered on top of a cluster. This was important since we observed an unstable tunneling current if the tip was not positioned exactly on top of the clusters, and additionally we observed a spatial energy shift for some structures in the tunneling spectra, as we will show below.

\( d(V) \) and \( d^2 dV/dV^2 \) curves were measured simultaneously with an open feedback loop, i.e. with a constant tip distance defined by the setpoint values of \( I \) and \( V \) before switching the feedback loop off. For the measurement of \( d^2 dV/dV^2 \) we used a lock-in technique, but obtained the same results by numerical differentiation of \( d(V) \) with a much lower signal-to-noise ratio. The use of the lock-in technique was important, since we had to use a very low setpoint current (\( I \leq 0.1 \) nA). For higher currents the clusters were pushed out of the pits during the spectroscopy scan, especially for larger cluster sizes. For this reason, we have so far only been able to measure STS data for cluster sizes \( h \leq 2 \) nm. The UPS signal from these small clusters was too weak to give sufficient statistics close to the Fermi level [6], so we do not yet present photoelectron spectra in direct comparison. The analysis of the UPS data for the 4d band indicates that, in this energy region, the electronic structure of the clusters deviates from bulk silver for cluster sizes \(<5 \times 10^5 \) atoms [7]. With UPS data for the surface state of an Ag(111) surface we checked that at \( T=5 \) K we get an energy resolution of 0.01–0.02 eV using the lock-in technique for the measurement of \( d^2 dV/dV^2 \) with a modulation voltage of 1–7 mV\(_{mod}\).

In Fig. 1 we show a topological image together with \( d^2 dV/dV^2 \) curves measured on the HOPG surface outside and inside the pit and at different positions on this cluster with \( h = 1.77 \) nm. For the small cluster sizes it was often also possible to measure inside the pit, since the clusters were grown at the edge of the pit leaving some area of the pit empty. The \( d^2 dV/dV^2 \) spectra of the HOPG surface show a V-shape which reflects the semi-metallic density of...
Fig. 2. \(dI/dV\) spectra collected for 14 different clusters with cluster heights given as measured with STM. The spectra are normalized to equal maximum \(dI/dV\) signal and shifted for better visibility; setpoint: \(V=0.5\ \text{V},\ I=0.09\ \text{nA},\ \text{modulation voltage} 7\ \text{mV}_{\text{rms}}\).

In Fig. 2 several \(dI/dV\) spectra are collected for 14 different clusters with the heights given as measured in the topological image. The height range \(h=1.1\text{–}2.1\ \text{nm}\) corresponds to mean cluster sizes \(N=90\text{–}600\ \text{atoms}\), given with a relative accuracy of 30% as discussed above. For most of the clusters all peaks were position-independent and we averaged spectra taken close to the top of the tip condition, but if it disappeared this did not change the other features of the spectra. The spectra on the cluster showed very pronounced peaks. Most of them (here e.g. at \(-0.28\ \text{V}\) and \(+0.4\ \text{V}\) in Fig. 1b), which we also observed in empty pits without a cluster at the edge. The presence of the small gap visible in the HOPG spectra at the Fermi energy was dependent on the states near the Fermi energy. Inside the pit, there are some small additional structures (at \(-0.1\ \text{V}\) and \(+0.4\ \text{V}\) in Fig. 1b), which we also observed in empty pits without a cluster at the edge. The presence of the small gap visible in the HOPG spectra at the Fermi energy was dependent on the
Fig. 3. \( \frac{dI}{dV} \) spectra measured with different setpoints on the same cluster \((h=1.17 \text{ nm})\); setpoints: \( I=0.09 \text{ nA} \) (both), \( V=0.5 \text{ V} \) (solid line), 1.0 V (dotted line). Note the different scales of the \( \frac{dI}{dV} \) axis.

cluster, but we included also the data to be discussed below in Fig. 4 for \( h=1.39 \text{ nm} \) presenting a single spectrum measured at one position on top of this cluster.

Spectra measured with different setpoints before the feedback loop had been switched off, i.e. with different tip–cluster distances, and taken on the same cluster, are compared in Fig. 3. We clearly observe that the structure of the spectrum is independent of the setpoint, i.e. of the tip–cluster distance. If we multiply one spectrum with a constant factor, which takes into account the different setpoints, we get identical spectra. We checked this for several clusters with different sizes.

Since we noticed that in some cases the energy of spectral features showed a spatial variation, we investigated this in more detail by measuring grids of points in a small area on top of this cluster. In Fig. 4 we display three spectra for the cluster with \( h=1.39 \text{ nm} \) in Fig. 2 focusing on the sharp peak feature which shows an energy shift similar to the peak at \(-1.2 \text{ V}\) in Fig. 1. For each of the voltages corresponding to the peak maxima we also present a spatial map of \( \frac{dI}{dV} \), which is bright at the positions where the peak has this energetic position. This shows that the energy shift is not arbitrarily caused by noise in the measurement, but has a systematic dependence on the spatial position.

Since the interpretation of STS data for clusters on a surface is very complex, as mentioned above, we cannot yet present a final interpretation of all spectral features. However, we can already extract several conclusions from our data. First, we can exclude that the spectral features measured on the clusters are caused by the pits in the HOPG...
surface, since $dI/dV$ spectra taken outside and inside the pits show only small differences (cf. Fig. 1b). Possible explanations for the additional structures in the pit are the quantization of electronic states confined in the pit [19] or defect-induced states [20]. A strong influence of the tip condition can also be excluded, since we observed the same features for the HOPG and the cluster spectra for different tips and for different conditions of the same tip.

The observed peak structures are not spaced equidistantly, and their distance and also the gap at the Fermi energy is not dependent on the tip-cluster distance (cf. Fig. 3), as would be expected for the Coulomb staircase of a two-junction system [12,21]. This is also consistent with the rather strong cluster-surface interaction, which we observed using high-resolution photoemission spectroscopy [6], because this will suppress the Coulomb staircase [11]. Instead we interpret the spectral features here as being caused by the quantized electronic structure of the cluster–surface system, leading to resonances in the transmission of the tunneling current. The general shape of some of our spectra looks similar to results obtained for Pt clusters on HOPG [8], but in our data the spectra change drastically with cluster size. A possible explanation for this difference is that, close to the Fermi level, Ag is a nearly free electron metal where the electron delocalization leads to strongly cluster-size dependent states, cf. the widely discussed jellium model. However, the influence of the d-electrons is not negligible, e.g. in optical experiments [22]. For the clusters measured here, the jellium model for a spherical particle should be considered rather than free-electron models for a two-dimensional film [23,24] because of the diameter-to-height ratio of 1.4. For small silver cluster anions, mass-selected in a free beam, photoelectron spectroscopy showed an electronic density of states which is rich in structure and shows a strong cluster size dependence [25]. In comparison, Pt is more bulk-like already for small cluster sizes [26]. With $\delta E = 2\pi B^2/(mk_F V)$, where $m$ is the electron mass, $V$ the cluster volume and $k_F$ the Fermi wave vector ($1.20 \times 10^{10}$ m$^{-1}$ for Ag) [15,27], we get as an estimation for the mean level spacing in a free electron system close to the Fermi energy $\delta E = 0.08-0.01$ eV for the range 90–600 atoms. This is the right order of magnitude, but the measured mean peak distances are larger than $\delta E$, which can be explained with a grouping or degeneracy of energy levels. In this sense $\delta E$ gives a lower bound for the level spacing. As an upper bound, the jellium model of a spherical cluster with $L = 5.42R$ as the average length of classical orbits responsible for the main-shell oscillations [28] results in $\delta E = h^2k_F/(2.71mR)$. This gives $\delta E = 1.5-0.8$ eV for the range of 90–600 silver atoms. The oblate cluster shape will alter this number, but in calculations the qualitative existence of electronic shells is found to be rather robust, e.g. in the case of surface roughness [29], a prolate spheroidal cluster shape [30], or the combined influence of small random cluster deformations and the inclusion of electron–electron interactions [31]. It is important to note that the shell structure is associated with a ‘bunching’ of electronic eigenvalues on an energy scale of the order $\delta E \times 1/N^{1/3}$ [32], while $\delta E \times 1/N$ for the spacing of individual energy levels. This expands the region between these two limits for increasing cluster size, which is illustrated in Fig. 5 with a graphical representation of $\delta E$ and $\Delta E$ plotted over the silver cluster size. But a simple jellium model will not be sufficient for the interpretation of our spectra, especially because of the additional influence of the surface to which the
cluster is bound. A strong cluster–surface interaction requires us to consider the cluster–surface system as a whole. This may also explain the observed spatial variation of some spectral features (cf. Fig. 4), which could be caused by a localization of the electron wave functions at e.g. the edge of the pit in which the cluster has been growing. 

In summary, we have presented an STS study at \( T = 5 \) K for silver clusters grown in nanopits on an HOPG surface. We identified the pronounced peak structure in the STS data as being due to a quantized electronic structure in the cluster–surface system. For some of the peaks a systematic spatial energy shift was measured. A conclusive interpretation of all spectral features observed cannot yet be given, but we expect that the combination of UPS and STS performed on the same samples will help in the interpretation of the spectra.

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References