Confined Shockley Surface States on the (111) Facets of Gold Clusters

I. Barke and H. Hövel*

University of Dortmund, Experimentelle Physik I, D-44221 Dortmund, Germany

(Received 30 November 2002; published 22 April 2003)

Combining low-temperature scanning tunneling microscopy and spectroscopy with high-resolution ultraviolet photoemission, we have revealed a confined Shockley surface state on the (111) facets of gold clusters with about $N = 10^4$ atoms grown in nanopits on highly oriented graphite. With tunneling spectroscopy, we observed energy dependent nodal patterns in the dI/dV maps, which are in quantitative agreement with the two-dimensional confinement of the surface state within the hexagonal facet area. The results indicate that the lattice of the ionic cores influences the electronic properties of the clusters significantly.

DOI: 10.1103/PhysRevLett.90.166801 PACS numbers: 73.22.–f, 68.37.Ef, 73.20.At, 79.60.Jv

The importance of electron confinement for the properties of metal clusters was observed in the mass abundance spectra of small alkali metal clusters with the appearance of electronic magic numbers which correspond to the closure of electronic shells [1]. The concept of electronic shells was extended to the range of a few thousands of atoms by the observation of supershell patterns in the cluster mass spectra [2]. For large clusters with several thousands of atoms, the mass spectra finally show geometric magic numbers, because the variations in the binding energies due to electronic effects become small compared to geometrical effects which drive the clusters towards well-defined crystalline structures [3]. But this does not exclude the existence of a quantized electronic structure due to the confinement of the conduction electrons also for large, faceted clusters. In this case, high-resolution spectroscopic techniques are needed for the detection of the small energy-level spacing. We used low-temperature scanning tunneling spectroscopy (STS) and high-resolution ultraviolet photoemission (UPS) for the study of the electronic structure of silver clusters on surfaces [4–6]. Here we present results for the extension of these studies to the case of gold clusters with sizes of up to 10^4 atoms on graphite. With the combined use of STS and UPS on the same sample, we reveal for gold clusters of this size a two-dimensional confinement of Shockley surface states on the (111) facets of the clusters in addition to the three-dimensional confinement of the electrons inside the cluster volume. Surface states can give a significant fraction of the density of states at certain energies, due to the large surface/volume fraction for clusters and the emergence of discrete modes. Therefore it will be important to include them in the discussion, in particular, for processes which are localized at the cluster surface and are influenced by surface states, e.g., adsorption processes [7] or growth phenomena [8,9].

The samples were produced and measured in a surface science facility, which combines scanning tunneling microscopy (STM) at $T = 5$ K and high-resolution ($\Delta E = 10$ meV) UPS with means for a surface preparation in a common ultrahigh vacuum chamber [10]. The preparation of the cluster samples followed the method of Ref. [11]. We produced nanometer sized pits with a depth of one monolayer (ML) on the surface of highly oriented pyrolytic graphite (HOPG) using the parameters as described in Ref. [6]. Then we deposited gold atoms with a rate of 2×10^{-3} ML s^{-1} at a substrate temperature of 350 °C. Previous measurements for this sample system using electron diffraction [12], STM [13], or UPS [6] showed that the gold clusters have a preferential orientation with the (111) plane parallel to the HOPG surface, different from silver clusters, which show a random orientation on the graphite [6]. This may be explained with differences in the growth process, e.g., the silver atoms were evaporated at lower substrate temperatures because otherwise the sticking coefficient was too low. But recent results for the structure of small gold clusters in the gas phase point to the fact that there is a more fundamental difference between silver or copper on the one hand and gold on the other, i.e., the more directional bonding for the latter metal, which leads to a preference for flat cluster structures [14]. With STM at $T = 5$ K (see Fig. 1), we measured the height distribution of the gold clusters

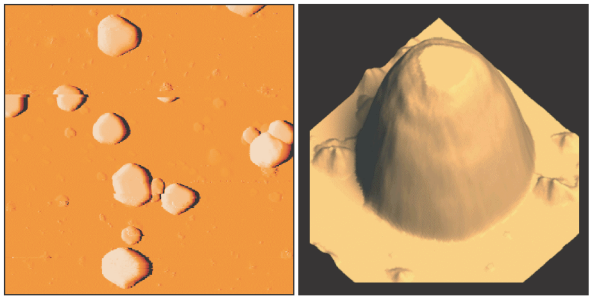

FIG. 1 (color online). Left image: Topographic STM image [(100×100) nm^2] of gold clusters on graphite (HOPG) produced by controlled condensation in nanopits. The STM data are numerically differentiated for a better visibility of the cluster shape. Right image: Three-dimensional display [(40×40) nm^2] of a single cluster. Area of the (111) top facet: $\Omega = 37$ nm^2 cluster height: $h = 3.9$ nm; $N = 1.5 \times 10^4$ atoms.

($h = 2.8 \pm 0.9$ nm) and we imaged the size and shape of the flat facets on top of the individual clusters. We measured nearly identical data for the tunneling current I with a variation of the tunneling gap, i.e., $I(z)$ on top of the clusters and on the HOPG (not shown), which indicates that the height measured with the STM will be close to the geometric height of the clusters. In contrast to the inflation of the total lateral cluster size [11], the imaging of the flat (111) facet is not hindered by the convolution with the tip shape. The cluster side facets are expected to be formed by (111) and (100) surfaces making an angle of 70.5° and 54.7° with the HOPG surface, respectively [15]. Therefore the cluster volume of the individual clusters can be calculated in a reasonable approximation using a truncated cone with the facet as the top surface and an angle of 60° to the HOPG surface.

STS data on individual clusters were taken at $T = 5$ K with an open feedback loop using a lock-in detection. Here we focus on the data for the largest clusters. An extended discussion for all cluster sizes is presented in a separate paper [16]. In Fig. 2(a), we present dI/dV data for a cluster with a height of $h = 3.9$ nm and an area $\Omega = 37$ nm^2 of the top facet. With this, we calculate $N = 1.5 \times 10^4$ for the number of gold atoms in this cluster. 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 or dark spots in the middle of the dI/dV maps correspond to a higher or lower dI/dV signal for the spectra taken for the center of the facet as compared to spectra averaged over the whole facet. An animated sequence of all 100 maps measured in the range −0.6 to +1.1 eV can be found in the supplementary material [18]. The number of nodes and antinodes increases with increasing voltage. In Fig. 2(b), we show another set of dI/dV maps measured on a second 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. As in Fig. 2(a), the energy positions of the maps correspond to maxima and minima in the center of the measured dI/dV spectra for this cluster (not shown). The observed patterns are very similar to the ones of Fig. 2(a), whereas the absolute energy positions differ in a systematic way (cf. Table I).

The dI/dV maps 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 [19]. 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 at $E_0 = -67$ meV for Ag(111). In our data, the lowest energy states with $E_1^a = -455$ meV [Fig. 2(a)] respective $E_1^b = -530$ meV [Fig. 2(b)] are close to the corresponding energy for the Au(111) surface, which was measured to $E_0 = -487$ meV with UPS [20]. We measured the same

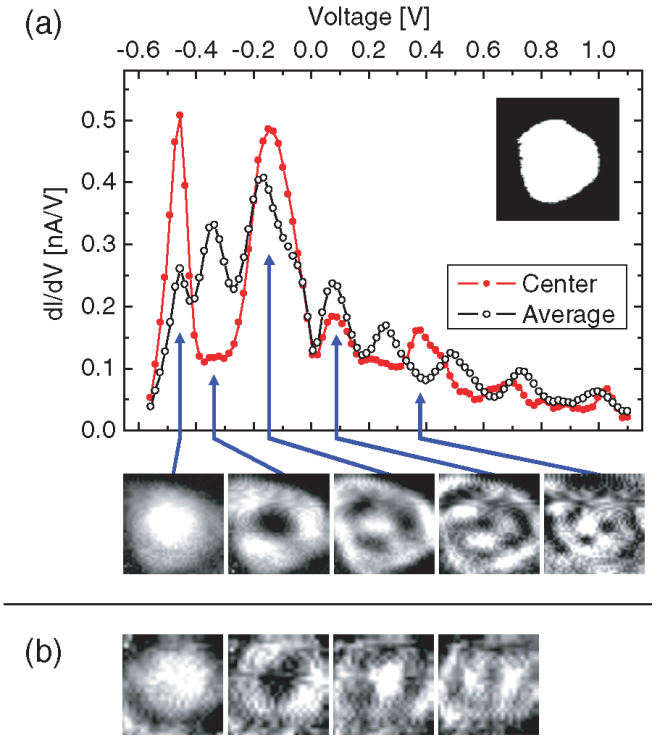

FIG. 2 (color online). (a) Scanning tunneling spectroscopy measured on the (111) top facet of the cluster shown in the right part of Fig. 1 ($\Omega = 37$ nm^2, $h = 3.9$ nm). Top: dI/dV spectra measured in the center of the facet (full dots) and averaged over the total facet area (open dots), respectively. The facet shape is shown in the inset [(10×10) nm^2]. Bottom: dI/dV maps [(4.5×4.5) nm^2] for five different voltages corresponding to the energy positions in Table I. (b) dI/dV maps [(5×5) nm^2] for a second cluster with $\Omega = 47$ nm^2 and $h = 2.5$ nm measured at four different voltages (cf. Table I). STS measured at $T = 5$ K with open feedback loop; setpoint: 1.1 V, 0.1 nA; modulation: 12 mV$_{\text{rms}}$.

TABLE I. Measured energy positions $E_n^{a,b}$ for the two clusters (a) and (b) from Fig. 2 and theoretical energy levels $E_n^{a,b,\text{calc}}$ for a 2D confined electron gas in a hexagonal facet using the theory and prefactors λ_n from Ref. [17]. See text for details. 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.

	λ_n	E_n^a	$E_n^{a,\text{calc}}$	E_n^b	$E_n^{b,\text{calc}}$
n	[eV nm^2]	[meV]	[meV]	[meV]	[meV]
1	0.7085	−455	(−455)	−530	(−530)
2	1.795	−336	−342	−420	−441
4	3.712	−148	−143	−270	−284
7	5.951	92	90	−105	−101
10	8.918	382	398	...	...

energy in the dI/dV curves on a Au(111) single crystal (not shown); however, the interpretation in this case is not as straightforward as for Ag(111) because of the effect of the $23 \times \sqrt{3}$ reconstruction [21].

But we want to stress the main difference to previous experiments for metal on metal systems, e.g., in Ref. [19], where the surface state exists in the Ag(111) surface, extending about 12 ML into the bulk [22], and the hexagonal 1 ML islands produce standing wave patterns due to scattering at the step edges [23–25]. 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 such as the occurrence of a gap in the surface projected band structure.

We have two other additional measurements showing characteristic surface state features. In Fig. 3, we show an averaged dI/dV spectrum measured on the first cluster with $N = 1.5 \times 10^4$ atoms for $V = -1.4 \cdots + 1.4$V. Because measurements with $|V| > 0.5$ V induced the danger of a tip change, 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. 2(a), one can observe a strong steplike structure at about -0.5 eV which is typical for a two-dimensional Shockley surface state [24,26], and its energy is close to the corresponding step for a Au(111) surface. Similar spectra were obtained for the second cluster with $N = 1 \times 10^4$ atoms, but not on other, generally smaller, clusters without such a pronounced nodal pattern on the facet [16]. Further evidence for the existence of a Shockley surface state on the large clusters is given by UPS spectra. The spectra in the left part of Fig. 4 were measured for the cluster sample with an angular resolution of $\pm 1°$. They show, on top of the characteristic Fermi level onset as described in Ref. [5], an extra peak at an energy about -0.5 eV for normal electron emission, i.e., $k_{||} = 0$, which disappears for angles $\pm 3°$ off normal emission. In the right part of Fig. 4, we compare this to the spectra of a Au(111) surface, measured for a film of bulk thickness on mica. The peak position in normal emission is similar, except for a shift of about 0.1 eV, to lower energies for the cluster sample [27].

We can describe the experimental STS data quantitatively using the model of Ref. [17], 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 I). The model of Ref. [17] gives $E_n^{\text{calc}} = E_0 + (\lambda_n/\Omega)(m_e/m^*)$ with the values of λ_n for a hexagonal confinement. For m^*, we use the effective mass $m^* = 0.26 m_e$ of the Au(111) surface state [20]. As the only free parameter, we adjust the surface state onsets $E_0^a = -528$ meV and $E_0^b = -588$ meV so that the energies $E_1^{a,b}$ 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 [17]. The shift of E_0 from -487 meV for a bulk sample [20] to $E_0^{a,b}$ is consistent with the UPS experiment (cf. Fig. 4), and it can be related to the shift of the surface state to higher binding energies for thin metal films [28] caused by the interaction with the substrate within the decay length. So the cluster height determines the surface state onset $E_0^{a,b}$, while the scaling for the peak positions of the confined states is given by the facet area Ω. In addition, possible shifts due to a film strain [29] must be taken into account. Based on our results, the extension of this model to larger cluster sizes should be feasible. However, we expect a failure below the range of validity for the bulklike description. Within this interpretation, the broad structure in the UPS spectra of Fig. 4 is given by the average over the first confined state

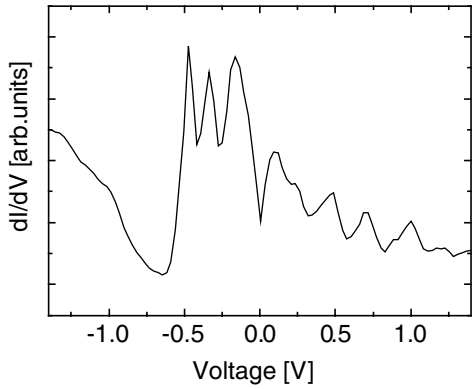

FIG. 3. Average over 14 single dI/dV spectra on different positions spread over the (111) facet for the same cluster as in Fig. 2(a) ($N = 1.5 \times 10^4$ atoms). STS measured for an extended energy range at $T = 5$ K with open feedback loop; setpoint: 1.5 V, 0.08 nA; modulation: 12 mV_{rms}.

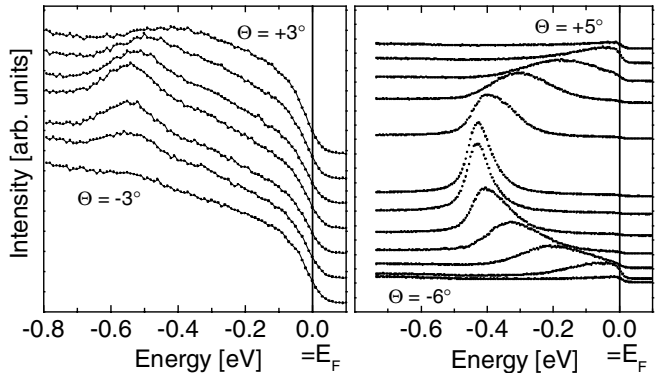

FIG. 4. Angle resolved photoemission ($h\nu = 21.2$ eV, $T \approx 50$ K, angular resolution: $\pm 1°$) measured for the sample with gold clusters on HOPG (left image), and for the (111) surface of a bulk Au film on mica (right image). The angle of electron emission Θ is varied in steps of 1° within the range given in the figures.

E_1 for different clusters. The disappearance of the peak structure for off normal emission can be explained as a remnant of the two-dimensional dispersion for a surface state. Similar effects occur at vicinal Au(111) surfaces for the direction perpendicular to the steps [30]. For E_n with $n > 1$, no corresponding structures are visible in the UPS spectra, probably due to averaging over a broad range of facet sizes and shapes.

Within a discussion in view of different bulk and thin film phenomena, the three-dimensional electron confinement in the faceted gold clusters can be thought to be composed of a one-dimensional confinement inside a thin film, and a two-dimensional confinement given by the lateral size of the clusters [16]. The first one leads to quantum well states for the electrons in the conduction band perpendicular to the surface [31,32]. But for a film thickness of ≈ 3 nm, the quantum well states show an energetic spacing of about 1 eV, which is significantly larger than the distance between the peaks observed in Fig. 2. For small clusters, the connection to different bulk phenomena will get less well defined and the electronic structure of clusters is better described by a three-dimensional electron confinement, e.g., with the well-known jellium model [33]. The observation of Shockley surface states, however, shows that this model has to be extended and the lattice of the ionic cores has to be included. Photoemission studies for thin metal films [32] indicate that the main features of the band structure for the direction perpendicular to the film thickness remain, though a thickness of only a few atomic layers would suggest an ill-defined $k_\perp$. This corresponds to the emergence of a Shockley surface state for faceted metal clusters with a diameter of a few nm, as presented here, which is connected to detailed bulk band structure properties.

The authors acknowledge support by the Deutsche Forschungsgemeinschaft (Ho-1597/3-3).

*Corresponding author.
Electronic addresses: hoevel@physik.uni-dortmund.de; http://e1.physik.uni-dortmund.de

[1] W. D. Knight *et al.*, Phys. Rev. Lett. **52**, 2141 (1984).
[2] S. Bjørnholm *et al.*, Z. Phys. D **19**, 47 (1991).
[3] T. P. Martin *et al.*, Chem. Phys. Lett. **172**, 209 (1990).
[4] H. Hövel *et al.*, Surf. Sci. **463**, L603 (2000).
[5] H. Hövel *et al.*, Phys. Rev. Lett. **81**, 4608 (1998).
[6] H. Hövel, Appl. Phys. A **72**, 295 (2001).
[7] N. Memmel, Surf. Sci. Rep. **32**, 91 (1998).
[8] K. Morgenstern *et al.*, Phys. Rev. Lett. **85**, 468 (2000); M. Giesen and H. Ibach, Phys. Rev. Lett. **85**, 469 (2000).
[9] N. Knorr *et al.*, Phys. Rev. B **65**, 115420 (2002); J. Repp *et al.*, Phys. Rev. Lett. **85**, 2981 (2000).
[10] H. Hövel *et al.*, J. Electron Spectrosc. Relat. Phenom. **88–91**, 1015 (1998).
[11] H. Hövel *et al.*, J. Appl. Phys. **81**, 154 (1997).
[12] H. Hövel *et al.*, Appl. Surf. Sci. **115**, 124 (1997).
[13] Y. J. Zhu *et al.*, Langmuir **18**, 5728 (2002).
[14] H. Häkkinen, M. Moseler, and U. Landman, Phys. Rev. Lett. **89**, 033401 (2002).
[15] K. Højrup Hansen *et al.*, Phys. Rev. Lett. **83**, 4120 (1999).
[16] H. Hövel and I. Barke, New J. Phys. **5**, 31 (2003).
[17] J. Li *et al.*, Surf. Sci. **422**, 95 (1999).
[18] See AIP Document No. E-PRLTAO-90-048314 for an animated sequence of all 100 maps. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from the ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.
[19] J. Li *et al.*, Phys. Rev. Lett. **80**, 3332 (1998).
[20] F. Reinert *et al.*, Phys. Rev. B **63**, 115415 (2001).
[21] W. Chen *et al.*, Phys. Rev. Lett. **80**, 1469 (1998).
[22] T. C. Hsieh, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **55**, 2483 (1985).
[23] Y. Hasegawa and Ph. Avouris, Phys. Rev. Lett. **71**, 1071 (1993).
[24] M. F. Crommie, C. P. Lutz, and D. M. Eigler, Nature (London) **363**, 524 (1993).
[25] S. Pons, P. Mallet, and J.-Y. Veuillen, Phys. Rev. B **64**, 193408 (2001).
[26] H. Hövel, B. Grimm, and B. Reihl, Surf. Sci. **477**, 43 (2001).
[27] The shift between the cluster data and the bulk data of Fig. 4 is increased by some 10 meV because we measured, probably due to film stress or a small angular misalignment, for the Au(111)/mica data $E_0 = -440$ meV slightly higher than given in [20].
[28] F. Patthey and W.-D. Schneider, Surf. Sci. **334**, L715 (1995).
[29] G. Neuhold and K. Horn, Phys. Rev. Lett. **78**, 1327 (1997).
[30] A. Mugarza *et al.*, Phys. Rev. B **66**, 245419 (2002).
[31] F. Patthey and W.-D. Schneider, Phys. Rev. B **50**, 17560 (1994).
[32] M. Milun, P. Pervan, and D. P. Woodruff, Rep. Prog. Phys. **65**, 99 (2002).
[33] W. Ekardt, Phys. Rev. B **29**, 1558 (1984).