Unoccupied states of individual silver clusters and chains on Ag(111)

A. Sperl, J. Kröger, N. Néel, H. Jensen, and R. Berndt
Institut für Experimentelle und Angewandte Physik,
Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany

A. Franke and E. Pehlke
Institut für Theoretische Physik und Astrophysik,
Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany

Size-selected silver clusters on Ag(111) were fabricated with the tip of a scanning tunneling microscope. Unoccupied electron resonances give rise to image contrast and spectral features which shift toward the Fermi level with increasing cluster size. Linear assemblies exhibit higher resonance energies than equally sized compact assemblies. Density functional theory calculations reproduce the observed energies and enable an assignment of the resonances to hybridized atomic 5s and 5p orbitals with silver substrate states.

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I. INTRODUCTION

Metal clusters at the nanometer scale which are supported by surfaces or thin films are currently of significant interest. Transport properties, catalytic efficiency, and selectivity depend strongly on the size of these assemblies. Moreover, understanding the influence of the substrate on the electronic structure of clusters is important for new cluster-based materials with tailored optical, catalytic, or magnetic properties. To this end, clusters may be decoupled from a metal surface by introducing an oxide thin film between the substrate and the deposited clusters.

Confinement of electrons to a small region leads to the formation of a discrete spectrum of their eigenstates. In condensed matter physics, spectroscopic studies of the discrete spectrum of individual samples has been rather demanding owing to difficulties in preparing and addressing suitable single particles. A major step forward was achieved with micro-fabrication techniques used to engineer semiconductor quantum dots, the levels of which could be resolved in a low temperature range by single-electron tunneling spectroscopy. Metals, however, owing to Fermi wavelengths which are of the order of a few tenths of a nanometer require extremely small particle sizes down to atomic-scale dimensions in order to render quantization phenomena observable. These sizes can be routinely obtained nowadays. Besides the required small cluster sizes the fabrication of assemblies with a narrow size distribution is another challenging experimental task. Several approaches to this goal are known, for instance, the manipulation of thermodynamic parameters which dictate a particular growth mode. While lithography or etching-based fabrication are exceptionally challenging techniques, buffer-layer-assisted growth was shown to lead to particularly narrow size distributions of deposited clusters. The "soft-landing" of mass-selected clusters requires a complex apparatus and faces the possibility of fragmentation, morphological changes and diversity.

Early scanning tunneling microscopy (STM) imaging of gold and silver clusters was reported by Abraham et al. and Sattler. Pioneering scanning tunneling spectroscopy studies of nanometer-sized clusters of gold and iron on GaAs(110) and of size-selected Si_{10} on Au(100) have been published already in 1989. Formation of states in the GaAs band gap was observed in the former cases while a variety of cluster images were obtained in the latter case despite the deposition of size-selected clusters. An important step forward was an experiment reported in Ref. Mass-selected clusters of Pt_{n} and Pd_{n} with 1 \leq n \leq 15 on Ag(110) were investigated using photoelectron spectroscopy. The authors observed size-dependent d states at binding energies around 2 eV below the Fermi energy. The line widths were observed to be size-dependent as well. From a comparison with total-energy calculations a chainlike shape of the clusters was inferred.

An ideal experiment enables the control of cluster size and shape at the atomic scale. Therefore, atom manipulation with the tip of a scanning tunneling microscope was applied in a variety of investigations, for instance, gold, manganese, iron, and cobalt dimers on NiAl(100), nickel dimers and chromium trimers on Au(111), copper chains on Cu(111) and manganese monomers to tetramers on Ag(111). Quantum confinement of electronic states to chains and islands was also revealed for homogeneous metallic systems.

Here we report on studies of electronic properties of silver assemblies fabricated by single-atom manipulation on Ag(111) using the tip of a low-temperature scanning tunneling microscope. As key results we obtain that unoccupied resonances exhibit energies whose actual values depend on the size and the shape of the atom clusters. In particular, linear and monotonically wide chains exhibit higher resonance energies than their equally sized compact counterparts. Moreover, confinement of the unoccupied resonance states to the linear assemblies is found. The energies of unoccupied reso-
nances of monomers, dimers, and a long silver chain are in agreement with density functional theory calculations.

II. EXPERIMENT

Measurements were performed with a custom-built scanning tunneling microscope operated in ultrahigh vacuum at a base pressure of $10^{-9}$ Pa and at 7 K. The Ag(111) surface and chemically etched tungsten tips were cleaned by argon ion bombardment and annealing. Individual silver atoms were deposited onto the sample surface by controlled tip-surface contacts as previously described in Ref. 38. Clusters with sizes ranging from one to eight atoms were fabricated by tip-induced movements. For tunneling resistances of $\approx 10^5 \Omega$, dragging of single silver atoms was feasible. Coalescence of adsorbed atoms (adatoms) to dimers up to octamers was accomplished by moving single adatoms close enough to the coalescence partner ($\approx$ one nearest-neighbor distance). We notice a propensity of silver adatoms to coalesce into compact assemblies rather than into linear clusters. For instance, adding an adatom to an already existing dimer in most of the cases resulted in a compact trimer rather than in a three-adatom chain. Silver chains containing more than 100 atoms were prepared by moving the tip toward the surface by 3 to 5 nm. Various surface dislocations were observed to result from this procedure. In particular, extraordinarily long and monatomically wide chains were found several hundreds of nanometers apart from the indentation area. Spectra of the differential conductance ($dI/dV$) were acquired by superimposing a sinusoidal voltage signal (root-mean-square amplitude 1 mV, frequency 10 kHz) onto the tunneling voltage and by measuring the current response with a lock-in amplifier. Prior to and in between spectroscopy of the clusters the tip status was monitored by giving a sharp onset of the Ag(111) surface state band edge in spectra of $dI/dV$. To obtain sharp onsets of the $dI/dV$ signal for the surface state and to image single adatoms with nearly circular circumference the tip was controllably indented into the substrate. Due to this in vacuo treatment of the tip

FIG. 1: (Color online) STM images of silver monomer, dimer, trimer, tetramer, and pentamer (from left to right) together with sketches of the proposed atomic arrangements (dark and bright circles depict substrate atoms and adsorbed atoms, respectively). Sample voltage and tunneling current were $V = 100 \text{ mV}$ and $I = 0.1 \text{nA}$. Image sizes: $2.1 \text{ nm} \times 2.1 \text{ nm}$ for Ag$_1$,...,Ag$_5$ and $3 \text{ nm} \times 3 \text{ nm}$ for the linear tetramer and pentamer.
we expect the tip apex to be covered with substrate material. All STM images were acquired in the constant current mode with the voltage applied to the sample.

III. THEORY

The total energy of the electronic groundstate and the Kohn-Sham eigenenergies have been calculated for the silver monomer and dimer configurations on Ag(111) using the Vienna ab initio simulation package (VASP)\textsuperscript{39,40,41}. Moreover, the Ag chain on Ag(111) has been calculated using the total energy package FHI96MD\textsuperscript{42}. Both program packages are based on density functional theory with the generalized gradient approximation (GGA) (monomer, dimer: PW91\textsuperscript{43}; chain: PBE\textsuperscript{44}) applied to the exchange correlation functional. These GGAs are expected to yield comparable results. For the monomer and dimer configuration the electron-ion interaction is treated within the framework of Bloechl’s projector augmented wave method (PAW)\textsuperscript{45,46}. For the calculation of the Ag chain a Troullier-Martins pseudopotential has been generated with the FHI98PP program. The monomer and dimer configurations have been modeled in a slab geometry comprising 14 layers of silver and a (4 × 4) or (5 × 4) surface unit cell, respectively. For the chain configuration the slab geometry consisted of 14 silver layers and a (9 × 1) surface unit cell. Perpendicular to the surface the periodically repeated silver slabs are separated by a vacuum region of approximately 1.7 nm, which has been the subject to convergence tests and proved to be sufficient. In all calculations presented here symmetric slabs were chosen such that the adsorption geometry is the same on both sides of the slab. The Kohn-Sham wave functions are expanded in a plane wave basis set, with a cutoff energy of 250 eV being sufficient in case of the PAW potential. A larger cutoff energy of 544 eV had to be used for the normconserving Troullier-Martins pseudopotential. The integrals over the Brillouin zone are approximated by sums over special \( k \) points\textsuperscript{47} using meshes consisting of 16, 9 and 6 \( k \) points in the complete first Brillouin zone for the monomer, dimer and chain, respectively. The local density of states (LDOS) has been calculated using the latter \( k \) point meshes in case of the monomer and dimer. Additionally, to accurately sample the dispersion of the unoccupied state close to the lower one-dimensional band edge, a mesh of 144 special \( k \) points\textsuperscript{47} in the first Brillouin zone has been used for the Ag chain. The Kohn-Sham wave functions at these additional \( k \) points have been calculated via so-called bandstructure runs, which are carried out at a frozen electron density from a previous self-consistent relaxation. The densities of states have been convoluted with a Lorentzian with a full width at half maximum of 10 meV (in a test calculation for an 8 layer slab). Using the normconserving pseudopotential and the PBE-GGA for exchange and correlation, the equilibrium lattice constant of silver is calculated to be 0.419 nm. The result is very similar (0.417 nm) when the PAW pseudopotential is used together with the PW91-GGA for exchange and correlation. These values are slightly larger than the experimental lattice constant of 0.409 nm, but the slight overestimate is consistent with other density functional calculations, e. g., for noble metals using GGA functionals\textsuperscript{48}. The slabs were set up using the respective theoretical lattice constants. The silver atoms of the outermost three layers on both sides of the slab as well as the adatoms were allowed to relax without constraints until the residual forces per atom were smaller than 7 × 10\textsuperscript{-4} Hartree/Bohr. The remaining layers of the slab were kept fixed at their ideal bulk positions. For the calculation of the monomer, one silver adatom is relaxed above the face-centered cubic (fcc) hollow site on both sides of the slab, corresponding to a coverage of one adatom per 16 surface atoms. For the dimer calculation two silver adatoms are relaxed above adjacent fcc hollow sites on both sides of the slab, corresponding to a coverage of one dimer per 20 surface atoms. The chain geometry consists of silver atoms adsorbed at next-neighbor fcc hollow sites in the direction of the chain.

| cluster | height (nm) | FWHM (nm) |
|---------|------------|-----------|
| Ag\(_5\) | 0.06       | 1.06      |
| Ag\(_2\) | 0.08       | 1.28      |
| Ag\(_3\) | 0.10       | 1.59      |
| Ag\(_4\) | 0.10       | 1.72      |
| Ag\(_5\) | 0.10       | 2.05      |
| Ag\(_6\) | 0.10       | 2.31      |
| Ag\(_7\) | 0.10       | 2.69      |
| Ag\(_8\) | 0.10       | 3.03      |

IV. RESULTS AND DISCUSSION

A. Compact and linear silver clusters: from monomer to octamer

Individual clusters with an exactly known number of atoms were fabricated by single atom manipulation. The results are presented in Fig.\textsuperscript{49}. Compact as well as linear assemblies were produced up to sizes of five and eight, respectively (Fig.\textsuperscript{49} shows clusters containing five atoms at maximum). We assume that individual silver adatoms
occupy the threefold coordinated fcc hollow sites of the Ag(111) lattice. Table I compares apparent heights and full widths at half maximum (FWHM) of linear assemblies with sizes ranging from a monomer to an octamer. Cross-sectional profiles of STM images were evaluated to this end. Per additional silver atom the length of the chains increases by 0.28 nm on an average, which is in good agreement with the nearest-neighbor distance of Ag(111). Starting from the trimer the apparent height is 0.10 nm for all subsequent silver assemblies.

In Ref. 54 copper clusters on Cu(111) were investigated at 5 K and the Cu$_2$ assembly exhibited a nearly circular shape in STM images. This observation was attributed to intracell diffusion, i.e., the dimer diffuses within a cell of adjacent hexagonal close-packed and fcc sites centered around an on-top site. In our case, however, the silver dimer on Ag(111) exhibits different dimensions along a close-packed direction (≈ 1.28 nm) and perpendicular to it (≈ 1.06 nm). We therefore conclude that intracell diffusion of a silver dimer adsorbed on Ag(111) plays a minor role.

Next we focus on unoccupied electronic states of the silver assemblies. Figure 2 shows a series of normalized dl/dV spectra acquired with the tip positioned above the center of compact clusters. The tunneling gap for spectroscopy was stabilized at 1 nA and 3.5 V for Ag$_1$, Ag$_2$, 3.0 V for Ag$_3$, and 2.5 V for Ag$_4$, Ag$_5$, Ag$_n$. Due to different tip-cluster distances for the various spectra we normalized the dl/dV data sets by the conductance I/V according to Refs. 51,52,53. The spectrum of clean Ag(111) is featureless up to ≈ 3.5 eV. A steady increase at higher sample voltages is attributed to field emission resonances. Thus, Ag(111) is a suitable substrate for observing unoccupied electronic states of clusters in the range of 0 to ≈ 3.5 eV. The dl/dV spectrum of a single Ag adatom exhibits a pronounced peak slightly below 3 eV. By performing spectroscopy in the vicinity of and on the single atom we found that the monomer resonance shows a spatial extension comparable to the size of the atom in STM images. These results suggest that the silver monomer exhibits a quasimolecular resonance. This interpretation is in accordance with observations for single Au atoms on NiAl(110)$_2$ and for Pd monomers on Al$_2$O$_3$ layers. Thus, the enhanced normalized differential conductance can be attributed to resonant tunneling into an empty state of the Ag atom. Indeed, our calculations reveal that this state is of sp character arising from the hybridization of atomic Ag 5p$_z$ orbitals with 5s admixtures localized at the adsorbate and silver substrate states. A typical wave function is shown in Fig. 3.

Spectra acquired on compact as well as linear clusters containing a higher number of atoms likewise exhibit a resonance whose energy shifts to lower values with increasing cluster size. Figure 3 summarizes the resonance energies for compact (triangles) and linear (circles) silver...
FIG. 4: Energies of unoccupied resonances as a function of cluster size. Resonance energies for compact (triangles) and linear (circles) assemblies are presented. (a) Experimental values. Error margins for the energies (≈ ±0.05 eV) are the standard deviation resulting from a statistical analysis of spectra of a variety of clusters. (b) Theoretical values from the tight-binding model described in the text (open circles and triangles), compared to ab initio Kohn-Sham eigenenergies (filled circles). The dashed line denotes the lower band edge of the dispersion of the chain states as obtained from density functional calculations. For each geometry the lowest tight-binding eigenenergy is given. The island configurations refer to those displayed in Fig. 1. The compact islands envelope the trimer, the tetramer, and the pentamer.

clusters of different sizes. The spectra were acquired atop the center of the assemblies. The resonance energies for compact clusters are lower than those for their equally sized linear counterparts. This observation is in agreement with our experience that in the course of atomic manipulation the silver adatoms exhibited the propensity to form compact rather than linear clusters. Therefore, compact clusters seem to be more stable reflecting the lower energy of their resonance. From Fig. 4a we further infer that for both cluster types the change of the resonance energy becomes less pronounced with increasing cluster size. For instance, the energy of the compact pentamer resonance is at ≈ 1.5 eV which already comes close to a compact assembly denoted Agₙ (n ≈ 10) in Fig. 2. Lagoute et al. showed for Cu adatom islands on Cu(111) an evolution of quasiatomic resonances to the two-dimensional Shockley-type surface state. In this study triangular Cu adatoms islands containing up to 15 atoms were investigated. In our case, an extrapolation of the energy data does not give the binding energy of the Ag(111) surface state which is at ≈ −70 meV. We propose that this result is due to the shape of our clusters which is triangular only for the compact trimer. We will see in the following paragraph that a long silver chain exhibits an unoccupied resonance whose energy is well above the Fermi level.

B. Monatomically wide silver chains

One-dimensional metal chains may exhibit interesting properties among which the Peierls distortion is probably most famous. This effect describes a modification of the spatial periodicity of the chain upon forming an energy gap around the Fermi level. In other words, the one-dimensional system gains energy by performing mechanical work for lattice deformation and by lowering its
electronic energy. For one-dimensional silver chains discussed here, however, no changes in the geometric structure were observed. The adsorption of silver atoms on Ag(111) leads to a hybridization of adatom orbitals with substrate electronic states and to resonances whose energies are far from the Fermi level (see Figs. 4–6). Consequently, small deviations in the chain geometric structure are not likely to modify the electron occupation of the resonance and therefore are ineffective in reducing the total energy of the silver chain. Nevertheless, a different combination of substrate and adatom material may lead to resonances close to the Fermi level and therefore may favor a Peierls transition.

Below we focus on electronic properties of monatomically wide silver chains. Figure 5 shows spatially resolved $dI/dV$ spectra acquired at different sites on a linear pentamer (see inset of Fig. 5). The $dI/dV$ spectrum taken atop the center of the assembly exhibits a single peak at $\approx 1.6$ eV (to be compared also with Fig. 4). By moving the location of spectroscopy toward the boundary of the linear cluster (spectra 2,...,8) a gradual trade of spectral weight from the resonance peak at $\approx 1.6$ eV to an additional peak at $\approx 2.3$ eV is observed. Moreover, compared to the resonance energy of $\approx 1.6$ eV observed atop the middle of the chain, at its ends this energy has shifted up to $\approx 1.7$ eV. We attribute the presence of an additional peak at the ends of the chain to confinement of the resonance to the linear cluster. Similar confinement effects for unoccupied resonances were observed for Au chains on NiAl(110) $^4$ and for Cu chains on Cu(111) $^30$.

How does the confinement evolve for chains containing an extremely high number of atoms? Starting from the linear octamer it became difficult to resolve confinement-related peaks in $dI/dV$ spectra, which may be related to overlap of neighboring peaks. Nevertheless, confinement was evidenced by localization of density of states at the ends of an extremely long chain, to be discussed next.

The length of the chain is $\approx 45$ nm and follows a close-packed direction of the hosting Ag(111) lattice. Consequently, the number of silver atoms is approximately 160. Figure 6 shows a normalized $dI/dV$ spectrum of the resonance in the middle of the chain. We extract an energy of $\approx 1.5$ eV and a FWHM of $\approx 0.6$ eV. Our DFT calculations reproduce the energy of this chain resonance (see an illustration of the wave function in Fig. 3b and...
In Figs. 7b and 7c we show the evolution of the apparent height and the FWHM close to the resonance energy.

In case of the monomer, a resonance predominantly derived from Ag sp$_z$ orbitals occurs at $\approx 2.3$ eV above the Fermi energy (see Fig. 3a). In case of the silver dimer, with Ag atoms occupying neighboring fcc sites, this resonance splits into a $p_z$ bonding resonance at $\approx 1.9$ eV and a $p_z$ antibonding resonance. The LDOS of the Ag chain is characterized by a one-dimensional band formed from an unoccupied $p_z$-like resonance as shown in Fig. 3b.

The lower band edge of this one-dimensional band is located at $\approx 1.3$ eV above the Fermi energy $E_F$ (as derived from the electronic eigenenergies). A peak arises at around $1.5 - 1.6$ eV. No upper band edge of the one-dimensional band was observed for energies below the work function of silver. Table II summarizes experimental and calculated resonance energies. Owing to the agreement between experiment and theory we interpret peaks in the $dI/dV$ spectra as the signature of $sp_z$- or $p_z$-like Ag adsorbate resonances and their electronic interaction with silver substrate states.

To compare experimental resonance energies with calculated results, we evaluated the LDOS at a position of $\approx 0.25$ nm atop the adsorbed Ag atom for the monomer and the chain. For the dimer configuration the LDOS was computed at approximately the same height atop the center of the dimer. The results are presented in Fig. 8. A similar LDOS for Cu chains on Cu(111) has been calculated by Stepanyuk et al.

In case of the monomer, a resonance predominantly derived from Ag $sp_z$ orbitals occurs at $\approx 2.3$ eV above the Fermi energy (see Fig. 3a). In case of the silver dimer, with Ag atoms occupying neighboring fcc sites, this resonance splits into a $p_z$ bonding resonance at $\approx 1.9$ eV and a $p_z$ antibonding resonance. The LDOS of the Ag chain is characterized by a one-dimensional band formed from an unoccupied $p_z$-like resonance as shown in Fig. 3b. The lower band edge of this one-dimensional band is located at $\approx 1.3$ eV above the Fermi energy $E_F$ (as derived from the electronic eigenenergies). A peak arises at around $1.5 - 1.6$ eV. No upper band edge of the one-dimensional band was observed for energies below the work function of silver. Table II summarizes experimental and calculated resonance energies. Owing to the agreement between experiment and theory we interpret peaks in the $dI/dV$ spectra as the signature of $sp_z$- or $p_z$-like Ag adsorbate resonances and their electronic interaction with silver substrate states.

We did not perform ab initio calculations for silver clusters of sizes larger than two atoms due to the large computational costs arising from the increasing size of the surface unit cell. However, we provide estimates for the electronic eigenenergies of larger clusters by means of a simple tight-binding model. The purpose of this estimate is to explain the energy shifts observed by tunneling spectroscopy semi-quantitatively. In our tight-binding approach the substrate is not considered explicitly, i.e., the islands are represented by free-standing two-dimensional clusters. We include one Ag $sp_z$ orbital per atom. There are only two free tight-binding parameters: the orbital energy $\epsilon_0$ and the next-neighbor transfer matrix-element $t_z$, which accounts for the direct interaction between nearest-neighbor Ag atoms and, implicitly, part of the interaction via the Ag substrate. All further interactions with respect to more distant atoms are neglected, as is the variation of the crystal-field energy shift of the orbital energy for different geometrical environments. As usual,
orbital overlaps are not accounted for explicitly.

The tight-binding parameters are consistently derived from our DFT results, i.e., the resonance energy of the monomer $\varepsilon_0 = 2.3\,\text{eV}$ (experimental value 2.9\,eV) and the binding energy of the Ag(111) surface state at $\bar{\Gamma}$ $\varepsilon_0 + \Delta\varepsilon = +0.05\,\text{eV}$ (experimental value $-0.07\,\text{eV}$) are reproduced by the tight-binding model. The quality of the tight-binding results can be estimated from comparison with the DFT Kohn-Sham eigenenergies and the chain shown in Fig. 4b. The lowest energy eigenvalue is given for each configuration. For further evaluation of the quality of the tight-binding model we notice that for the effective mass $m^*$ of the surface state we obtain 0.8\,m_e (m_e is the free electron mass) from tight-binding calculations to be compared with a DFT value of 0.39\,m_e and an experimental value of $(0.42 \pm 0.02)\,m_e$. The effective mass of the $s_p$ resonance at the one-dimensional Ag chain is 1.2\,m_e in our tight-binding approach to be compared with a value of about 0.6\,m_e derived from the dispersion of the Kohn-Sham eigenenergies close to $\bar{\Gamma}$. Most probably, the overestimate of the effective mass by a factor of two in both cases may be partially due to the fact that no parameter describing the crystal-field energy shift is included in the tight-binding Hamilton operator giving rise to an inaccurate value of the transfer parameter.

Nevertheless, the simple tight-binding approach provides all qualitative trends for the cluster eigenenergies (see Fig. 4b). Compact clusters have lower eigenenergies than equally sized linear assemblies and the trimer exhibits a lowest electronic eigenenergy which is close to the lower band-edge of the infinite chain.

V. SUMMARY

Size-selected silver clusters were fabricated by tip-assisted single-atom manipulation on Ag(111). Unoccupied electronic resonances exhibit energies which are characteristic of size and shape of the silver assemblies. In particular, the resonances of linear clusters have higher energies than the resonances of equally sized compact clusters. For both types of clusters the resonance energy shifts toward the Fermi energy with increasing cluster size. These observations are qualitatively in agreement with a tight-binding model of the clusters. Calculations based on density functional theory model the energies of monomers, dimers, and monatomically wide infinitely long chains. The resonances are of sp character and arise from Ag $5p_z$ orbitals (with $5s$ admixtures) which are localized at the adsorbate atom and hybridize with silver substrate states.

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* Electronic address: kroeger@physik.uni-kiel.de

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