Observation of shell effects in nanowires for the noble metals Cu, Ag, and Au

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We extend our previous shell effect observation in gold nanowires at room temperature under ultrahigh vacuum to the other two noble metals: silver and copper. Similar to gold, silver nanowires present two series of exceptionally stable diameters related to electronic and atomic shell filling. This observation is in concordance with what was previously found for alkali metal nanowires. Copper, however, presents only electronic shell filling. Remarkably we find that shell structure survives under ambient conditions for gold and silver.

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I. INTRODUCTION

Evidence shows that the stability of metallic nanowires is strongly correlated to their electrical properties. Applying a free electron model to a cylindrical nanowire, the electronic free energy as a function of the radius shows an oscillating spectrum with minima that represent stable nanowire configurations due to shell filling. Experimental evidence of shell filling in metallic nanowires was reported for alkali metal nanowires by Yanson et al. Similar to metal clusters, alkali metal nanowires present two series of stable diameters, due to electronic and atomic shell filling. In our previous work we reported evidence that shell filling effects are also present in gold nanowires. In this paper we extend the study to the other two monovalent noble metals: silver and copper. Noble metal nanowires are more suitable for applications, being less reactive than the alkali metal nanowires. It would be of great importance to be able to predict and control nanowire stability. Noble metals differ from alkali ones in the shape of Fermi surface (nearly spherical vs almost perfectly spherical) and also in the bulk packing (fcc vs bcc). To some extend the free electron model can be applied also to noble metal nanowires, as was proven successfully for noble metal clusters. We present evidence that, similar to gold, silver and copper nanowires show certain exceptionally stable diameters of the same origin: shell filling. Firstly, we see electronic shell effects in all three metals. Secondly, the atomic shell effect appears only in gold and silver nanowires. Silver, however, is exceptional, regarding the more pronounced shell structure as well as the small variation in the peak positions. Remarkably, we find that for gold and silver some of the stable diameters survive even under ambient conditions, which is a big step in the direction of possible applications.

II. EXPERIMENTAL TECHNIQUE

The stability analysis of the noble metal nanowires is done by investigating electrical conductance using a mechanically controllable break junction (MCBJ) method. A bulk polycrystalline metal wire is notched circularly and fixed on a substrate. By bending the substrate with a piezoelectric element the wire breaks at the most sensitive point, the notch. By retracting the piezoelement the contact between the two bulk pieces will be remade. Controlling the voltage on the piezoelectric element, one can finely control the dimensions of the contact with atomic resolution. In the process of thinning down, the contact experiences different metastable configurations, depending on the atomic rearrangements in the nanowire and its close vicinity.

Since we search for stable diameters, the atoms need to have sufficient mobility to select the most favorable among all possible metastable configurations. One way to enhance their mobility is by increasing the thermal energy. The optimal temperature is a significant fraction of the melting temperature but one has to take into account that for nanowires the melting temperature is strongly suppressed. For example, Hwang and Kang find in a calculation for copper nanowires of 34 atoms in cross section a melting temperature of 590 K (compared to bulk value 1357 K). On the high end, the optimal temperature is limited by the reduced lifetime of the metastable states at elevated temperatures. Bürki et al. give an estimate of the relevant activation energies, which are more than a factor of 2 higher for the noble metals as compared to the alkali metals.

We have developed a new MCBJ technique adapted for use at elevated temperatures in ultrahigh vacuum (UHV), described in detail elsewhere. We have improved our previous design such that our new sample holder has a tray of six bending beams with a sample mounted on each that we can independently measure, and avoid breaking the vacuum for each new wire in this way.

The conductance is measured at constant bias voltage, recording the current with a current-voltage converter using a digital to analog card of 16 bits resolution. The contact is thinned down starting from about 100 000 to about 1 second. Here, G0=σ2h/2 is the quantum of conductance and 100G0 roughly corresponds to ∼100 atoms in cross section. Different breaking times in the range of 10 ms to a few minutes and different dimensions of the starting contact were tested. A typical conductance trace follows a step-like pattern, with plateaus for metastable configurations of the contact and jumps resulting from atomic rearrangements in the vicinity of the contact. In order to find only the preferred diameters from all metastable configurations, we use a statistical analysis, by adding many conductance traces in a histogram. The conductance scale is divided into about 600 bins, and a histogram is build from a few thousand scans. A peak in the histogram corresponds to a preferred, reproducible configuration of the contact.
and $R_k$ positions in units of $18G_0$ at the peak of 1000 peaks have a relatively low amplitude, the maximum being previously reported for gold atomic contacts. We see that these peaks are situated close to certain conductance values. In the low conductance range of gold and copper it varies between different measurements. The slope for silver is found at about 150G0, while for gold and copper it varies between different measurements on values of 7G0, 10G0, and 12G0 for gold and 10G0, 14G0, and 18G0 for copper.

III. RESULTS

A. Electronic shell effects

Figure 1 presents a conductance histogram recorded at room temperature under UHV (UHV-RT) using a bias voltage of 100 mV. The histogram reproduces our previously reported result. One can see a sequence of distinct peaks at certain conductance values. In the low conductance range peaks are situated close to 1G0, 2G0, and 3G0; the conductance for 1, 2, and 3 atoms in cross section, as reported previously for gold atomic contacts. We see that these peaks have a relatively low amplitude, the maximum being at the peak of 10G0.

For the regime of thick nanowires the conductance is related to the nanowire radius by a semiclassical formula for a ballistic nanowire with circular cross section,

$$G = g G_0 \approx G_0 \left[ \left( \frac{k_F R}{2} \right)^2 - \frac{k_F R}{2} + \frac{1}{6} + \cdots \right],$$

with $k_F R$ the Fermi wave vector, $g$ the reduced conductance, and $R$ the radius of the nanowire. When we plot the peak positions in units of $k_F R$ as a function of peak index we get a linear dependence, illustrated in the inset of Fig. 1 with a slope of $\Delta k_F R = 1.06 \pm 0.01$, similar to the one obtained for alkali metals. This is an indication that the peaks in the conductance histogram are due to electronic shell filling: the nanowire chooses such diameters that give minima in the electronic free energy.

We now find similar periodic patterns for silver and copper nanowires as one can see in the histograms of Fig. 2. The periodicity of the peaks is similar to gold. Thus for silver and copper the slope is $\Delta k_F R = 0.98 \pm 0.01$. The maximum spectrum amplitude for silver is found at about 15G0, while for gold and copper it varies between different measurements on values of 7G0, 10G0, and 12G0 for gold and 10G0, 14G0, and 18G0 for copper.

B. Atomic shell effects

Sometimes a new series of peaks appears in the histogram as we can see in Fig. 3 (top), that was reported in our previous work recorded for gold in UHV-RT. This is related to a geometrical effect also present in clusters, namely, atomic shell filling. Certain nanowires are more stable when they adopt a crystalline order with smooth facets, such as to obey minima of surface energy. This effect is expected to appear at larger diameters than electronic shell filling. Silver nanowires present this new series of stable diameters even more pronounced than gold does, with peaks up to conductance values of 80G0 (see Fig. 3). However, for copper we have not observed distinct atomic shell effect peaks.

The crossover between electronic and atomic shell effects is in most of the cases around 10G0 for gold, and at about 15G0 for silver but it can vary around this value between different measurements. This variation can be due to local crystalline orientation, a parameter that we cannot control during measurements. The crossover value is in some histograms hard to determine since in addition to the consecutive series of peaks having atomic shell effect periodicity, electronic shell effect peaks appear to be superimposed.

We observe that during a particular measurement, after repeated cycles of making and breaking the contact, an evo-
A transition from atomic shell effect periodicity to electronic shell effect appears, as one can see in Fig. 4. Curves 1, 2, and 3 are histograms recorded during the same measurement containing 5000, 8000, and 20,000 consecutive scans. A smooth positive background was subtracted from the histograms for better clarity. Firstly we can see that some peaks having atomic shell effect periodicity in histogram 1 gradually decrease their weight in histogram 2 until they disappear in histogram 3. Secondly we see that in histogram 3 the peaks vanish above 30\(G_0\), while in histograms 1 and 2 they are visible up to about 40\(G_0\). Finally in the histogram 3 we get peaks that have electronic shell effect periodicity. This transition from atomic to electronic shell effect was reported previously also for alkali metals, and can be due to an increase in mobility of the atoms during repeated cycles of elongation/compression of the nanowire, which can damage the faceting. Another possible reason may be that during repeated indentation the crystalline orientation of the nanowire or of the connecting electrodes changes, not being favorable anymore for faceting.

C. Experiments under ambient conditions

Figure 5 (top) shows a conductance histogram for gold recorded at room temperature under ambient conditions, constructed from 2000 and 10,000 individual consecutive traces, respectively, giving evidence of electronic shell filling. The bin size was 0.13\(G_0\) (gold) and 0.08\(G_0\) (silver) and the bias voltage of 100 mV (gold) and 20 mV (silver). The insets show the peak positions, converted to \(kF\), as a function of peak index with a slope \(\Delta k_F R = 1.00 \pm 0.01\) (gold) and \(\Delta k_F R = 1.06 \pm 0.02\) (silver).
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and gold. The relative intensity of the peaks is different from those under UHV. The maximum amplitude is shifted to lower conductance values with respect to UHV. Moreover the peak at about $1G_0$, commonly attributed to a single-atom contact,\textsuperscript{12} has a much higher amplitude than under UHV. It has been shown by Hansen et al.\textsuperscript{13} that a one-atom contact is hardly stable under UHV-RT, due to the high mobility of the atoms. However, under ambient conditions adsorbates decrease the atom mobility, resulting in an enhanced stability of small contacts. This may explain also the previous results for gold atomic contacts obtained at RT in air.\textsuperscript{8} In our conductance histograms we see that only the electronic shell effect survives in air. This is not unexpected since the atomic shell effect is a surface effect; therefore, adsorbed species modify the surface energy and are expected to damage the facetting.

Copper does not show shell effect peaks in air. The dominant feature is a broad peak close to $1G_0$, as previously reported.\textsuperscript{18} Since copper is known to be the most reactive of the three noble metals, the absence of shell structure can be caused by fast oxidation of the contact.

IV. DISCUSSION

A. Comparison with low temperature histograms

Conductance histograms for gold at low temperatures reported in the literature typically show only the range of low conductances that is dominated by a peak near $1G_0$, attributed to a one-atom contact; see, e.g., results on gold at liquid helium temperatures.\textsuperscript{9} Peaks can be distinguished only up to $3G_0$ followed by a flat tail. For copper and silver conductance, histograms recorded at helium temperature are similar to gold having a dominant peak at or just below $1G_0$, followed by two additional peaks of lower intensity.\textsuperscript{19} There is a major difference in the origin of the low temperature peaks compared to our UHV-RT histograms. At low temperature the atoms are frozen in configurations that have a certain conductance value. In UHV-RT measurements, atomic mobility plays an important role and the nanowire can self-organize such to find the most stable configuration. Therefore, the peaks in our data reflect preferred stable diameters, and not preferred conductance as in the case of low temperature histograms.

B. Comparison between the three different noble metals

In Fig. 6 we plot the averaged values of the peak positions in histograms showing electronic shell structure recorded from different independent measurements for gold, silver, and copper. We observe that the peak positions are very close to each other for the three metals. There are variations for the gold peaks indexed 6 and 9. It is possible that one peak is missing in the histograms because of the supershell modulation of the peak amplitudes,\textsuperscript{20} as will be explained later. The standard deviation is quite low, showing that the stable diameters can be reproduced very well in different measurements. We believe that the small shifts that are observed come from variations in the conductance due to backscattering on defects near the contacts.

![FIG. 6. Averaged peak positions and their standard deviations obtained from conductance histograms of independent measurements for Ag (11 measurements; squares), Cu (12 measurements; circles), and Au (5 measurements; triangles). Results of the stabilized jellium model considering a circular cross section are also included (crosses) (Ref 12).](image)

C. Electronic shell effect theory

The periodic pattern present in our histograms in Figs. 1 and 2 due to minima in the electronic free energy of the nanowire as function of elongation. We compare our peak positions with the theoretically predicted stable diameters reported by Ogando et al.\textsuperscript{12} The theoretical model used is called a stabilized jellium model and considers the nanowire as an infinitely long cylinder taking into account the average valence electron density of the metal. With this assumption the energy oscillations as function of radius are obtained, having minima due to shell filling. These minima agree well with the experimentally obtained stable diameters for the three metals in question, as we can see in the insets of Figs. 1 and 2 (triangles) and in Fig. 6 (crosses).

The physical mechanism leading to a magic series of diameters is best illustrated using a semiclassical approach. The electron moves classically in the circular cross section of the wire. The stable diameters are determined by closed orbits inside the cylindrical walls of the wire. The orbits that proved to have the most significant contribution for alkali nanowires are the diametric, triangular and square orbits.\textsuperscript{9,20} The oscillating frequencies that result from these orbits are $1/\Delta k_R R=0.64$ for diametric orbit and $1/\Delta k_R R=0.83$, $1/\Delta k_R R=0.90$ for triangular and square orbits. A beating effect known as supershell effect appears due to the superposition of the diametric orbit with the higher frequency orbits (triangular and square). In order to separate the oscillating frequencies in the experimental histograms we perform a Fourier transform. Since we are interested in only the oscillatory part of the spectra in Figs. 1 and 2 we subtract a smooth background. The Fourier transform for Au (Fig. 7, top) shows a broad peak centered at a frequency of $1/\Delta k_R R=0.92$. This value is somewhat higher than what is expected from the superposition of the triangular and square orbits. This deviation can be seen as due to conductance lowering due to backscattering on defects in or near the nanowire. This correction seems to be contact size dependent, as seen by the fact that the conductance is lowered, but the calculated radii of the contact are still linear with peak index, as seen in the insets of Figs. 1 and 2. Indeed the slope is somewhat lower than that obtained from the stabilized free.
length is about six times larger than the main Fermi wavelength, for gold and copper. Filling of the states in the neck will have a period six times larger than the one resulting from the states in the belly. The silver Fermi surface has even smaller deviations, resulting in a wavelength and a period of resulting oscillations of density of states eight times higher than those in the belly. Moreover, the contribution of the states of the necks to the total density of states is relatively small. Therefore, in a good approximation Au, Ag, and Cu may be considered free electron metals. Our assumption is supported by electronic structure calculations for the quantum modes in nanowires of Na and Cu.  

D. Comparison to magic numbers of noble metal clusters

We compare also the values for the preferred nanowire diameters with the magic radii in clusters (circle symbols in Figs. 1 and 2, obtained from the number of atoms in a cluster, \(N\), as \(k_FR=1.919N^{1/33}\)). We see that the agreement is very good. This is at first sight unexpected due to the difference of symmetry, which is spherical in the case of clusters and cylindrical for nanowires. However, we first note that the gross features of distribution of zeros for spherical and cylindrical Bessel functions are nearly identical for not too large diameters. The difference between cylindrical and spherical geometries is expressed mostly in the relative weight of the various semiclassical orbits. For nanowires the diametric orbit is expected to have a strong contribution in the oscillation spectrum while for clusters it is negligible. Since we have very little influence of the diametric orbit, possibly as a result of surface roughness, we obtain about the same oscillation period as for noble metal clusters.

E. Atomic faceting

At larger diameters, the surface energy becomes more important than the free energy. The oscillation amplitudes of the electronic free energy have a 1/R dependence while the ones for surface energy are roughly constant. A crossover between the two is experimentally observed by the change in the oscillation period. We propose a model for nanowire faceting starting from the crystalline order that we have in bulk: fcc for all three noble metals. We assume that the nanowires form along the [110] axis having a hexagonal cross section with four (111) facets and two larger (100) ones (inset of Fig. 3). The filling of each individual facet will give a stable diameter. There has been another proposed cross section of the nanowire with octagonal symmetry.23 We have chosen the hexagonal cross section along the [110] orientation supported by high resolution transmission electron microscopy (HRTEM) observations.24,25 These experiments provide evidence that the bulk crystalline order survives in gold and copper atomic contacts. The atomic arrangement of the nanowires obtained by means of the Wulff construction reveal that the growth occurs preferentialy along the crystalline directions [110], [111], and [100], with the first one being more favorable for growing long nanowires. Our model is further supported by Monte Carlo simulations that confirm that for the process of thinning down of a nanowire the [110] direction is a preferred orientation for forming long and
stable nanowires with a faceted structure. The expected periodicity of stable diameters is \( \Delta k_F R = 0.476 \). This value is very close to the experimentally observed periodicity for gold \( \Delta k_F R = 0.40 \) and even closer for silver \( \Delta k_F R = 0.46 \). Silver also has the largest number of atomic shell effect peaks, as one can see in Fig. 3.

Previous results on copper nanowires in UHV-RT have been reported by combining HRTEM and MCBJ. From independent imaging and conductance measurements of copper nanowires, Gonzales et al. suggest that a stable pentagonal configuration occurs having a conductance of \( 4.5G_0 \).

In most of the cases (7 out of 10 measurements) our conductance histograms for copper show a peak at \( 5G_0 \), and very rarely at lower values between \( 4G_0 \) and \( 5G_0 \). Similarly for silver the peak position is close to \( 5G_0 \). However for gold we reproducibly see a distinct peak close to \( 4G_0 \). This peak was tentatively attributed to a quadrupolar distorted nanowire that gold may have preference to form. Such distortions would be most likely when the surface tension is low. The surface tension for gold lies in between that for Cu and Ag, which seems to rule out this interpretation. We propose that the \( d \)-bonding character for gold that also gives rise to the formation of atomic chains may play a role for the smallest contacts.

Kondo and Takayanagi reported the formation and imaging of suspended multishell helical gold nanowires with diameters ranging from 0.6 nm and length of 6 nm. Such anomalous atomic arrangements in nanowires, referred to as “weird wires,” had been predicted from model calculations by Gülsersen et al. Recently the conductance of these structures was calculated by first principle methods. We compare in Fig. 1 the calculated values of the conductance for the multishell helical wires with our peak positions. One can observe that the period for the first few peaks is close to the period of the calculated helical nanowire conductances, although their values do not fully coincide. However, at higher conductances the bars start to get closer together in contrast to the peaks in the histogram. We do not exclude the formation of helical nanowires, but we believe the peaks in the histogram are due to shell effect considering the agreement with the theoretically predicted period. The reason why helical wires form in the experiment by Kondo et al. and not in ours is likely to be attributed to the different experimental methods for forming the nanowires.

V. CONCLUSION

We have evidence that electronic shell filling influences the formation and stability of all three noble metal nanowires: gold, silver, and copper. At larger diameters the atomic shell effect is dominant and appears in gold and silver but was not observed in copper. We observe that the shell structure is the most pronounced in silver nanowires. Regarding the electronic shell structure the Fourier spectrum reveals that the main contribution comes from the superposition of triangular and square orbits. Free electron model predictions of stable radii due to the shell effect agree well with our results. Predicted values of conductance for gold elliptically distorted nanowires agree with the experimental peaks. Our stable diameters are in good agreement with the magic diameters of noble metal clusters. Together with the results for alkali metals, we thus conclude that shell effects are generally observed for monovalent metals. The effect is sufficiently robust that it can be observed under ambient conditions for gold and silver.

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