Conductance of Atomic-Sized Lead Contacts in an Electrochemical Environment

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Atomic-sized lead (Pb) contacts are deposited and dissolved in an electrochemical environment, and their transport properties are measured. Due to the electrochemical fabrication process, we obtain mechanically unstrained contacts and conductance histograms with sharply resolved, individual peaks. Charge transport calculations based on density functional theory (DFT) for various ideal Pb contact geometries are in good agreement with the experimental results. Depending on the atomic configuration, single-atom-wide contacts of one and the same metal yield very different conductance values.

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Charge transport through nanostructures presently constitutes a highly active area of research, also due to its relevance for the further miniaturization of electronic devices [1]. Regarding atomic-sized metallic contacts, different experimental techniques have been developed for their fabrication, e.g. mechanically controllable break junctions (MCBJs) [2], modified scanning tunneling microscopes (STMs) [3], electromigration [4], and electrochemical methods [5, 6]. While in MCBJ experiments and STM-based setups atomic-sized contacts are formed by plastic deformation of the contact area, the advantage of the electrochemical deposition method is the absence of mechanical strain during contact formation, resulting in corresponding differences in conductance histograms.

Conductance histograms of s-valent metals, such as gold, silver, or copper, have been analyzed extensively [1, 7, 8], showing a preference for multiples of $G_0 = 2e^2/h$, with the peak at $1G_0$ being a very robust feature. As it is known that the chemical valence plays an important role for electron transport [9, 10], conductance histograms for multivalent metals may consequently show a very different shape [1, 8].

In this work, Pb will serve as a model system for multivalent metals. For Pb a broad peak between $1G_0$ and $3G_0$ was observed in conductance histograms based on the MCBJ technique [11, 12]. During stretching of the junctions, the plateau regions of the conductance traces commonly exhibit a negative slope as a result of the mechanical strain [9, 13]. With electrochemical techniques we have recently fabricated atomic-scale silver contacts with a high thermal and mechanical stability [14], and exploited this for constructing gate-controlled atomic switches [15]. In this work, we study charge transport through atomic-sized Pb contacts in experiment and theory. The conductance histogram is compared to the literature and theoretical results for ideal contact geometries. In the DFT-based calculations we explore both “single-atom” and “dimer” geometries with a single atom or a chain of two atoms in the narrowest part of the junction, respectively. For these configurations we consider orientations of the semi-infinite electrodes along the three main crystallographic directions, namely $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$.

Our experimental setup is illustrated schematically in Fig. 1. Since lead oxidizes under ambient conditions, the electrochemical cell is shielded in an inert gas chamber. Before starting with the electrochemical deposition, the chamber is thoroughly streamed with Ar. In this way, a practically oxygen-free environment is created for the growth of the atomic-sized Pb contacts. For their fabrication, two working electrodes (WEs) made of gold and separated by a gap of approximately 50 nm are prepared. They are covered with an insulating polymer coating except for the immediate contact area to minimize ionic conduction. Two lead wires (0.5 mm diameter, 99.998% purity) are used for the quasi-reference electrode (RE) and the lead counter electrode (CE). The potentials of the

Figure 1: (Color online) Schematic diagram of the experimental setup. Pb is deposited and dissolved electrochemically in the narrow gap between two gold working electrodes (WEs) on a glass substrate, and the conductance of the contact is measured simultaneously. The potentials of the WE with respect to the lead reference electrode (RE) and the lead counter electrode (CE) are set by a potentiostat.
WEs with respect to the RE and the CE are set by a computer-controlled potentiostat. The electrolyte consists of 1mM Pb(NO₃)₂ + 0.1 M HNO₃ in bi-distilled water. For conductance measurements an additional voltage of -12.9 mV is applied between the two WEs. To exclude possible specific effects of the gold WEs, contacts were also grown using Pb electrodes, yielding comparable results.

To fabricate the lead contact within the gap between the two WEs, a potential of 10-20 mV is applied to the RE. While lead is deposited in the junction, we monitor the conductance between the WEs. After contact deposition, the contact is dissolved again by setting the electrochemical potential of the RE to a value between -18 mV and -36 mV, and closed again by choosing the potential between 6 mV and 15 mV. By continuously repeating this procedure, conductance-time traces are recorded for a large number of opening and closing processes at a sampling rate of 50 ms.

Two typical conductance-time traces obtained for contact closing (deposition) and opening (dissolution) are shown in the inset of Fig. 2. The plateau regions in the traces are quite flat in general. This fact can be explained by the lack of mechanical strain during the electrochemical growth process, in contrast to contacts fabricated with the MCBJ or STM techniques, where mechanical deformations are involved [9, 10, 13]. The dissolution curve exhibits two plateaus at around 2.8G₀ and 1.4G₀. These values are consistent with the range of the rather continuously decreasing last conductance plateau, as reported in Refs. [9, 13]. The main panel of Fig. 2 shows the conductance histogram, plotted with a bin-size of 0.05G₀. It represents the data from 1.5·10⁶ conductance terraces in the range between 0 and 20G₀ for both deposition and dissolution from 64 different samples, each terrace being stable longer than 200 ms. The structure of the histogram with its most dominant peak at 1.4G₀ differs clearly from those obtained with the MCBJ approach, where only a single, broad peak was observed between 1G₀ and 3G₀ and no detailed structure within this peak could be resolved [11, 12]. Here, most probably due to the lack of mechanical strain and structural defects within the junction area, a detailed substructure is resolved within this peak, demonstrating the advantages of the electrochemical fabrication method. The peak position at 1.4G₀, however, is consistent with the results reported in Refs. [11, 12]. Additional peaks in the conductance distribution are found at 1G₀, 2G₀, and 2.8G₀. In the range from 3G₀ to 6G₀, the distribution is quite flat and shows a low broad maximum centered at around 4.8G₀.

In order to understand better the experimental findings, we have performed a theoretical analysis of charge transport through various Pb contacts. We describe their electronic structure at the level of DFT and determine the conduction properties within the Landauer approach using Green’s function techniques. Employing the RI-DFT module of TURBOMOLE 5.9 [16], we use BP86 as exchange-correlation functional [17, 18] and the standard basis set “def-SVP” of split-valence quality augmented with d-like polarization functions [19]. An effective core potential efficiently deals with the innermost 78 electrons [20]. Out approach is described in detail in Ref. [21]. Let us note that we determine parameters for the description of the electrodes from a spherical fcc cluster composed of 429 Pb atoms. The lattice constant for this cluster is set to the experimental value of 0.495 nm. The calculation yields \( E_F = -3.76 \text{ eV} \) for the Fermi energy, a value roughly corresponding to the experimental work function of 4.25 eV [22].

We investigate two types of junction configurations, namely single-atom and dimer contacts (Figs. 3 and 4). For these we study different crystallographic orientations of the electrodes, namely \( \langle 100 \rangle \), \( \langle 110 \rangle \), and \( \langle 111 \rangle \). The electrodes are oriented along the z axis, the direction of charge flow. Such geometries are believed to be responsible for the first peak in conductance histograms of metals under ultra-high vacuum conditions. We consider only ideal geometries, where all atoms are located in the positions of the fcc lattice. The extended central clusters of Ref. [21] used for the description of the contacts, are composed of around 300 atoms. To keep the numerical effort manageable, their point group symmetry is exploited.

Results for the single-atom contacts are displayed in Fig. 3. From the transmission at the Fermi energy, we obtain conductances of 2.7G₀, 5.3G₀, and 2.8G₀ for the \( \langle 100 \rangle \), \( \langle 110 \rangle \), and \( \langle 111 \rangle \) directions, respectively. At first glance, the conductance for the \( \langle 110 \rangle \) direction is surprisingly high. However, as is visible in Fig. 3(d), this contact should better be considered as a “five-atom” contact due to the additional bonds resulting from the small distance between atomic layers. Therefore, we will henceforth refer to single-atom contacts as those for the \( \langle 100 \rangle \) and \( \langle 111 \rangle \) directions. For the latter two structures, the transmission at \( E_F \) is dominated by three transmission
channels. In each case, the non-degenerate channel is of sp-like character, while the two degenerate ones are p_x- and p_y-like. The local density of states (LDOS) of the atom in the narrowest part of the constriction illustrates further the dominant role of the 6s and 6p states for conduction.

Due to the directional character of transport the point group symmetries relevant for the classification of transmission channels in terms of irreducible representations are C_{4v}, C_{2v}, and C_{3v} for the structures with ⟨100⟩, ⟨110⟩, and ⟨111⟩ orientations, respectively, while their geometrical point groups are D_{4h}, D_{2h}, and D_{3d}. Degeneracies of channels, present for the ⟨100⟩ and ⟨111⟩ configurations, are therefore removed for ⟨110⟩. This fact will be more clearly visible for the dimer junctions with their lower conductance, but the same point-group symmetries, which we shall discuss next.

In Fig. 3 we illustrate the evolution of the conductance and of the total energy as a function of the distance d between the tip atoms for all the dimer contacts. All other distances are kept fixed in the stretching process. At the point of minimum total energy, conductances are 2.3G_0, 1.6G_0, and 2.8G_0 for the ⟨100⟩, ⟨110⟩, and ⟨111⟩ contacts, respectively. As naively expected, the conductance exhibits a monotonous decay with d for ⟨100⟩ and ⟨110⟩. For ⟨111⟩, however, it stays rather constant. From an analysis of the LDOS of one of the chain atoms, we find that this is due to the p_x and p_y states, which move into resonance. As mentioned before, degeneracies of conduction channels are lifted for the ⟨110⟩ orientation as compared to the other junction configurations.

The peaks at 1.4G_0 and 2.8G_0 in our histogram of Fig. 2 are consistent with our theoretical results for single-atom and dimer structures. This indicates that the contacts observed in the experiment resemble ideal lead junctions without strong contaminations or structural defects, since they would lead to deviations from these conductance values.

The experimentally observed, pronounced peak at 1G_0 is not predicted by the conductance calculations described above. However, as the contacts are in an aqueous electrochemical environment, small molecular species working as bridges between the two atomic-scale Pb electrodes, such as traces of H_2O, O_2, or H_2O, might play a role [12, 23, 24]. Alternatively, ionic lead species could be taken into account, where specific transport channels of the junction are selectively suppressed. The interpretation of the peak at 1G_0 as a result of the conductance quantization of a free electron gas in a geometrical constriction, as observed in semiconductor heterostructures [25, 26] and s-type metals [1], appears as an oversimplification for multivalent metals [12, 27].

An alternative explanation of the peaks at 2G_0 and 2.8G_0 would be their interpretation as replicas of those at 1G_0 and 1.4G_0 with twice the value. Although geometries with parallel atomic wires were observed for STM-fabricated gold contacts [28], no indications for the formation of similar structures exist for lead so far.

Our analysis of transport using DFT is in agreement with theoretical results reported in Ref. [13]. Employing a simpler tight-binding parametrization for describing the
electronic structure and considering only the single-atom contact oriented along the (111) direction, the authors report the same conductance of $2.8G_0$. Keeping the central atom fixed, they find that the conductance stays practically constant when the junction is stretched, similar to our observations for the (111) dimer structure. They argue that the negative slopes of the conductance plateaus before contact rupture would require the inclusion of spin-orbit interactions. While such relativistic effects are considered in our calculations only in an effective manner through the core potentials [20], our results show that the dependence of the conductance on distance is strongly geometry-dependent.

To conclude, the high thermal and mechanical stability and low strain in our electrochemically fabricated atomic-sized lead contacts makes it possible to resolve sharp conductance peaks and detailed substructures within the broad first peak in the conductance histograms obtained with MCBJ or STM techniques. The theoretical analysis of transport within our DFT approach yields junction geometries compatible with the peaks at $1.4G_0$ and $2.8G_0$ and allows to attribute them to neutral single-atom and dimer contacts of Pb. The results demonstrate that the conductance of Pb contacts with a single-atom-wide constriction depends crucially on the contact geometry.

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