Zero Bias Anomalies in Electrochemically Fabricated Atomic-Scale Metal Junctions

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ABSTRACT

We present transport measurements of metal nanojunctions (MNJs) made by solution-based electrochemistry. Similar methods have been proposed for making nanoelectrodes in molecular electronics experiments. Understanding the properties of the metal at the atomic scale is essential for analyzing any molecular conduction measurements employing such electrodes. Measurements in MNJ structures reveal suppression of the conductance as the temperature is lowered. The size of this zero bias anomaly (ZBA) varies strongly with the electrochemistry and the geometry of the resulting MNJ. As junctions approach the atomic scale, the ZBA becomes nonperturbatively large (approaching 100%). We present evidence that this reflects a large density of states suppression in the disordered leads.

Keywords: Metal point contact; nanojunction; electrodeposition; zero bias anomaly; nanoscale electrodes

1 INTRODUCTION

Electronic transport in metallic nanojunctions (MNJ) can probe correlations, quantum coherence, and disorder at the atomic scale, and are the subjects of much current research. Clean MNJs are fabricated in ultrahigh vacuum (UHV) by the break junction method, using scanning tunneling microscope[1] or microfabricated structures[2]. Phenomena examined in such clean systems include conductance quantization[3], suppression of shot noise[4] and conductance fluctuations[5] at conductance plateaus, and mechanical stability[6] of metals at the atomic scale.

Simultaneously, several investigators[7]–[10] have proposed using electrochemically prepared electrodes with nanometer separations in molecular electronic devices. However, metal deposited from solution may be highly disordered by grain boundaries, incorporation of ionic impurities, and adsorption of impurities onto surfaces. To ascertain the importance of this kind of disorder in nanoscale electrodeposited gold, we have created a series of MNJs by electrodeposition. Cross-sections range from a few nanometers to the atomic scale. We have examined the electrical transport properties of these systems from room temperature down to 1.8 K. This temperature range is significant, since disorder physics can be obscured at high temperatures. Similar structures have shown conductance quantization and Ohmic behavior at room temperature[7], [8]. Prior to this work, no low temperature measurements on such disordered, chemically fabricated systems have been reported.

In all MNJs examined with conductances less than $30 \times 2e^2/h \equiv G_0$ where G_0 is the conductance quantum, we find suppression of the junction dc conductance near zero bias at low temperatures. Junctions deposited from standard alkaline buffer solution [7] with room temperature conductances $<\sim 1G_0$ have zero bias anomalies (ZBAs) approaching 100% conductance suppression as $T \to 0$. Junctions made with an HCl-based technique[10] show much smaller ZBAs.

We demonstrate experimentally that the large ZBAs result from nonperturbative corrections to the local density of states (LDOS) of the disordered metal leading to the nanojunction. Since perturbatively small LDOS corrections in disordered metals have long been ascribed to dynamically screened electron-electron interactions[12], it is tempting to consider the large ZBA as related to this same disorder physics.

2 SAMPLE FABRICATION

The fabrication process has been reported in detail elsewhere[11], and is summarized here. We fabricate gold source and drain electrodes on thermally oxidized $p+$ silicon substrates. E-beam patterning defines electrodes with tip widths $<\sim$ 200 nm and a separation of $\sim$10 nm. The electrodes are e-beam evaporated, 2.5 nm Ti, 25 nm Au, and 20 nm Al_2O_3. A pair of electrodes is shown in Fig. 1. A rectangular auxiliary electrode[9] 0.1 mm^2 is simultaneously evaporated.

Additional Au is then electrochemically deposited onto these electrodes to produce a nanoscale junction for study. We employ two different chemistries, and find that the low temperature nanojunction properties are influenced by the choice of protocol. Devices exhibiting large ZBAs are made by a technique (labeled "M" for the authors of Ref. [7]) using an aqueous solution of 0.01 M $KAu(CN)_2$ in a buffer of 1 M $KHCO_3$ and 0.2 M KOH (pH $\approx$ 10). During deposition the source-drain conductance is monitored by a lock-in amplifier.

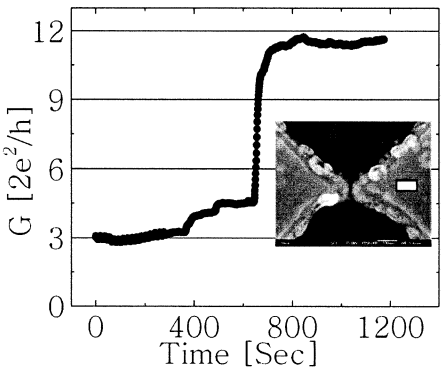

Figure 1: Steps in junction conductance as atomic configurations shift during growth. Inset: micrograph of alumina-coated starting electrodes; scale bar = 100 nm.

The alumina layer limits the area where gold may be deposited by isolating the solution from all but the edges of the electrodes[13].

Conductance steps on the order of G_0 are observed (Fig. 1) when a metallic connection is formed between the source and drain electrodes. The electrochemistry is halted at a specified source-drain conductance. The deposition solution is removed by dry nitrogen gas. Many nanojunctions are destroyed at this step through spontaneous breakage or coalescence.

At room temperature, few-channel junctions can be stable for as long as tens of minutes, longer than clean junctions made in ultrahigh vacuum[2], [3], [6]. Discrete spontaneous conductance changes are often observed, and are much more rare once the sample temperature is lowered. These conductance changes and their strong temperature dependence suggest that our MNJs comprise a small number of gold atoms that can diffuse readily at 300 K.

We have also used an the chemical approach of Boussaad and Tao[10] (labeled "BT"). In this method, the existing gold is reconfigured by solvation and redeposition. The chemistry is simpler, involving only 0.2 M HCl solution, with no salts or buffering agents. These junctions exhibit much smaller ZBA conductance effects than the those produced through the M procedure.

3 MEASUREMENTS

Surviving junctions are studied in a variable temperature crystat. We have measured ten nanojunctions with room temperature conductances from 0.5 to 200 G_0. Thermal contraction effects appear to be negligible during temperature sweeps, except as discussed below. The lithographic electrodes have sheet resistances of $\sim 1\ \Omega$, consistent with the resistivity of gold and the thickness of the films. Standard lock-in techniques are used in a quasi-4 terminal configuration to measure the nanojunction differential conductance as a function of temperature, dc bias voltage and magnetic field. At room temperature, all nanojunctions we measure are Ohmic at biases up to 200 mV. Samples with $G(300\ K) > 100\ G_0$ exhibit metallic behavior over the accessible temperature range, 300 K to 1.8 K.

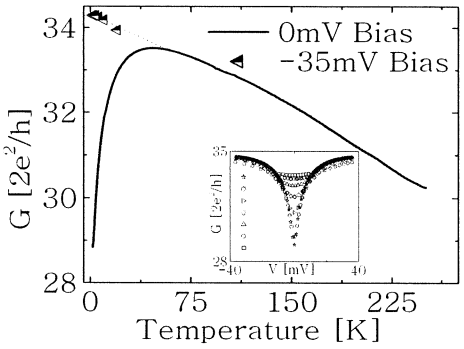

Figure 2: (a) Temperature sweeps of dI/dV at low and high dc bias in a relatively large junction; (b) Bias sweeps at various T.

3.1 High conductance junctions

All nanojunctions with $G(300\ \mathrm{K}) <\sim 30G_0$, however, exhibit a suppression of the zero-bias differential conductance as the temperature is reduced below 50K. For one highly conducting junction ($G \sim 30G_0$) referred to as Sample A, this suppression is roughly logarithmic in temperature, as shown in Fig. 2a. Metallic behavior in $dI/dV(T)$ is recovered when the differential conductance as a function of T is measured with a -35 mV dc bias. Assuming that the transverse size of the nanojunction is smaller than the elastic mean free path of electrons, one can use the Sharvin method[15] to estimate the junction cross-section from the conductance. The result is approximately 4 nm.

Figure 2b shows bias voltage sweeps of the differential conductance of Sample A at various temperatures below 30 K. The apparent ZBA becomes more pronounced as the temperature decreases, reaching about 15% when $T \rightarrow 1.8\ K$. All samples with $G(300\ \mathrm{K}) <\sim 30G_0$ made using the M method show substantial low-T ZBAs. We also find ZBAs in comparable MNJs made using the BT method, but those are much smaller, about 0.2% at 1.8 K. Perpendicular magnetic fields as large as 8 T do not affect these ZBAs.

To understand the ZBA we observed in Sample A (Fig. 2), we consider two analyses. The first is that of Weber *et al.* in Ref. [16], used to analyze electronic transport in gold quasi-2d diffusive nanobridges with dimensions 80 nm× 80 nm × 10 nm. Weber *et al.* ascribe the ZBAs they observe in such nanobridges to singular corrections to the electronic density of states (DOS) in their devices. Altshuler, Aronov and Lee (AAL) com-

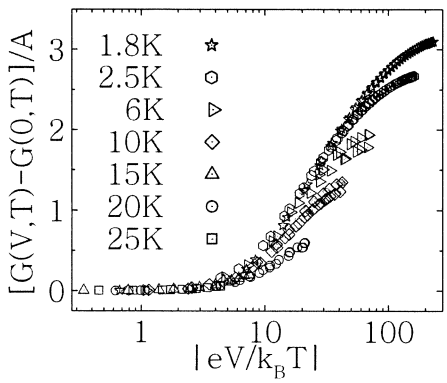

Figure 3: Scaled ZBA data, showing collapse to one curve at low values of T, V, similar to that seen in Ref. [16].

pute these corrections perturbatively as electron-electron interaction effects in disordered metals[12]. Weber, *et al.* model the conductance of their nanobridge by a two-terminal Landauer-Buttiker formula, generalized to include the AAL interactions. They predict $[G(V,T) - G(0,T)]/A = f(eV/k_{\rm B}T)$, where A is a constant determined by the zero bias conductance, $(G(0,T) = G_* + A\ln(T))$, and $f(x)$ is a functional form determined by the 2d diffusive nanobridge. Figure 3 shows our data scaled as suggested by this equation. At $|eV/k_{\rm B}T| > 1$, $f(x)$ is roughly logarithmic, qualitatively consistent with the data of Weber *et al.* We do not expect quantitative agreement, since our nanojunction is not a 2d diffusive system and should therefore possess a different $f(x)$.

A second analysis is suggested by the work of Golubev and Zaikin[17], a general theory of Coulomb interactions in transport through a coherent region. For systems with $G/G_0 >> 1$, they also predict a ZBA in the differential conductance that varies logarithmically in $|eV/k_{\rm B}T|$, consistent with our data. Both analyses suggest that electron-electron interactions in the disordered junction and leads are responsible for the ZBA shown in Fig. 2.

3.2 Atomic scale junctions

Nanojunctions with atomic scale cross-sections and correspondingly lower room temperature conductances exhibit significantly larger ZBAs at low temperatures. We now present evidence that the large ZBAs in atomic-scale junctions are caused by *nonperturbative* corrections to the local density of states of the disordered leads arising at low temperatures and atomic length scales.

Figure 4 shows conductance of an atomic-scale nanojunction (Sample B, G(T=300K) = 1 G_0) as a function of temperature cycling. During the initial cool down (branch I), above 50 K, G is nearly temperature independent, while below 50 K we begin to see a substantial drop as in previous samples. However, upon cooling to 15 K the conductance of the nanojunction spontaneously increases by about 0.6 G_0. As the temperature is further reduced, the conductance of the nanojunction continues to decrease logarithmically in T, but from a higher conductance. Upon warming (branch II), the nanojunction remains in this higher conductance state, like a sample with room temperature conductance near 2 G_0. However, at 220 K the conductance of the nanojunction spontaneously decreases by about 0.85 G_0, returning to its original value. Further temperature cycling (branch III) showed no additional hysteresis.

These discrete changes confirm the atomic size scale of the nanojunction. The addition of a single conducting channel upon decreasing temperature presumably occurs as thermal contraction slightly moves the source and drain closer together. Similarly, the loss of the channel on warming supports this view, with thermal expansion now stretching the junction. This hysteresis behavior is reminiscent of that seem in mechanical break junction measurements of atomic point contacts. From this discrete switching, we infer that our nanojunctions are true atomic size connections between two disordered metal leads, in contrast to the "dirty" break junction analyzed in Ref. [14].

We then warmed the sample back to 300 K and took the sample into the ambient environment. When the nanojunction was returned to the measurement chamber, we observed a decrease in the room temperature conductance of the nanojunction by about 0.5 G_0, leading to branch IV. Next, we turned on a red LED in the measurement chamber at 2 K, and the conductance of the nanojunction increases by around 0.2 G_0. The temperature dependence of the differential conductance of this fifth configuration (branch V) nearly overlaps with the initial temperature trace. We find that all $G(V = 0,T)$ curves of this device can be made to collapse onto a single curve by multiplying each branch by a constant (inset).

For each conductance branch described above, bias sweeps were performed to measure the ZBA several temperatures. Figure 4b shows the conductance versus bias voltage plots at 2 K, 10 K, and 20 K of this nanojunction in its various configurations. Note that the conductance change for this ZBA is nearly 75%. With the same scaling factors used to collapse the $G(V = 0,T)$ branches onto a single curve, the bias sweep data also collapse, as shown. The entire data set, $G(V,T)$, is of the form $A \times g(V,T)$, where A is a constant characteristic of a particular configuration of junction atoms, and $g(V,T)$ is a single function applicable to *all* conductance branches. We hypothesize that the size and form of $g(V,T)$ is related to the amount of disorder in the leads, and that disorder is fabrication method and instance dependent.

We analyze these ZBAs using two approaches. First, we consider unremarkable source and drain densities of

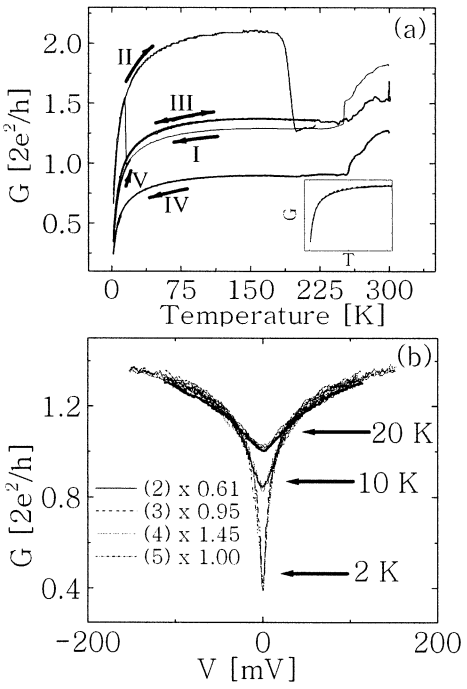

Figure 4: (a) Temperature cycling of a $G(300\text{ K}) \approx 1\ G_0$ junction,showing discrete, hysteretic behavior due to atomic scale reconfigurations of the junction; (b) ZBA data from the junction configurations of (a), all collapsed by scaling factors obtained from $G(V = 0, T)$.

states, and an energy dependent (but temperature independent) transmission function $T_0(E)$ connecting the source and drain. In this approach, temperature dependence arises from the thermal smearing of the source and drain Fermi distributions. No choice of $T_0(E)$ reproduces the observed rapid temperature dependence of $G(V = 0, T)$ in this model.

An alternate analysis is based on tunneling LDOS measurements. A temperature and energy independent "tunneling" conductance G_0 is assumed; instead the LDOS for the leads is assumed to be a function of both temperature and energy, $\nu(E, T)$. Within this model, with a single functional form for $\nu(E, T)$ possessing two fit parameters, the temperature and bias dependence of $G(V, T)$ can be described well for four such samples, including Sample B[11].

These ZBA imply that electrochemically fabricated nanoelectrodes may not be optimal choices for use in molecular electronics measurements. The DOS of the electrodeposited leads can have a nontrivial temperature and energy dependence when probed on the atomic scale. Deconvolving the electronic properties of a candidate molecular device from those of the leads is therefore likely to be a complicated task.

We have employed a streamlined, reproducible method based on electrodeposition to fabricate atomic size nanojunctions with room temperature conductances ranging from 0.5 G_0 to 200 G_0. Differential conductance measurements on these junctions while varying temperature and bias voltage reveal zero bias anomalies at low temperatures. We attribute our observation to corrections to the local density of states in the disordered metal leads. The disorder in the leads is presumably due to the particular solution-based nature of the electrochemistry used.

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