Nanometer-spaced platinum electrodes with calibrated separation

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We have fabricated pairs of platinum electrodes with separation between 20 and 3.5 nm. Our technique combines electron beam lithography and chemical electrodeposition. We show that the measurement of the conductance between the two electrodes through the electrolyte provides an accurate and reproducible way to control their separation. We have tested the robustness of the electrodes by applying large voltages across them and by using them to measure the transport properties of Au nano-clusters. Our results show that the technique reliably produces metallic electrodes with a separation that bridges the minimum scale accessible by electron beam lithography with the atomic scale.

Modern chemistry has produced a large variety of objects perfectly defined on a molecular level that are of interest for the development of nano-scale electronics 1. Examples are metallic and semiconducting clusters, conjugated organic molecules and fullerenes. The investigation of their individual properties and their use in practical circuits requires the ability to interface these objects with the macroscopic world. In particular, to perform electrical measurements, contacts must be made to single nano-objects. Over the past few years ingenious methods have been introduced to fabricate metallic leads with a separation on the nanometer scale 2-5. However, a simple, fully controllable and reproducible technique capable of bridging the dimension scale accessible by (e)-beam lithography (≈ 20-50 nm) with the atomic scale (≈ 0.1-1 nm) is still lacking.

Recently, a technique (hereafter referred to as ‘electrochemical narrowing’) combining conventional lithography and electrochemistry has allowed the fabrication of metallic electrodes with atomic separation 6-8. In this technique, metal electrodeposition on two planar electrodes (fabricated by conventional means) is used to reduce their separation. In-situ monitoring of the conductance between the two electrodes provides the desired control. The simplicity and robustness of the process as well as its flexibility (e.g., electrodes fabricated in this way can be readily integrated with electrostatic gates) are some of its key aspects.

So far, only the working principle of electrochemical narrowing has been demonstrated but many important issues remain to be solved. In particular, no optimization of the process and not even of the metal to be deposited have been performed yet. Also, and more fundamentally, it is unclear whether the monitoring of the conductance can be used to control the inter-electrode separation on a length scale larger than 1-2 nanometers and, if so, whether it is possible to calibrate this control method with sufficient accuracy and reproducibility.

Here, we report a systematic study of nano-electrode fabrication by means of electrochemical narrowing. We show that by optimizing the electrode layout and the control circuit we can monitor the inter-electrode conductance for separations up to 20 nm. By stopping the electrodeposition process at predefined conductance values we reproducibly obtain the same electrode separation with a ∼ 10% error. We have found that the use of Pt allows for high reproducibility and high stability of the electrodes (in comparison to deposition with Au). We have tested the quality of the electrodes by performing electrical measurements on individual Au nano-clusters with a diameter ranging from 20 to 5 nm.

Details of the electrode fabrication are as follows. With e-beam lithography, we define the ‘large’ separation electrodes on thermally oxidized silicon wafers by evaporating 7 nm of Ti and 25 nm of Pt. After lift-off, the initial separation is between 40 and 80 nm (see Fig. 1). The samples are then dipped in a buffered solution of hydrofluoric acid (AF 87.5-12.5, LSI Selectipur, Merck) for 20 seconds which etches approximately 30 nm of SiO2. As a result, the extremities of the electrodes are free-standing. Such free-standing contacts reduce the possible channels of parallel conduction on the substrate surface. The sample layout away from the electrode extremities is also of importance. As compared to Ref. 7 we have reduced the electrode area that is in contact with the electrolyte, which improved the monitoring sensitivity.

Electrodeposition of Pt is performed in an aqueous solution of 0.1 mole of K2PtCl4 and 0.5 moles of H2SO4 8. Contrary to gold, the quality of electrodeposited Pt is very sensitive to the initial conditions of the electrode surface. Gold can readily be plated from a cyanide bath containing gold ions without any pre-treatment of the electrodes. When following the same procedure with Pt, the material grows with a very rough morphology (i.e., grains of random size nucleates at random locations). This morphology does not allow the fabrication of nanoscale contacts.

To obtain a smooth Pt surface we first clean the evaporated platinum electrodes in an O2 plasma. We then put the electrodes in solution and apply a square wave signal with respect to the counter electrode for a few seconds. The voltage changes from -1.8 V to +0.7 V in periods of 400 ms for a few seconds. Pt is then electrodeposited by biasing the two electrodes at 420 mV with respect to the counter-electrode (a Pt wire). This process produces uniform Pt grains, whose size is less than 6 nm. Such a small grain size is normally not obtained with Au.

Monitoring the inter-electrode conductance during
FIG. 1: Upper left corner: the initial separation of the electrodes as defined by electron beam lithography and lift-off is 60 nm. Figures I, J and K show electrodes fabricated by stopping the electrodeposition process when the monitor current was 30, 90 and 140 nA respectively. The electrode separations corresponding to these values are 16, 10 and 3.5 nm.

growth is done using a lock-in amplifier (see Fig. 2a). Compared to Ref. 6 the monitoring circuit has been improved. First, the resistor used to measure the ac monitor current \(I_m\) is larger (10 kΩ) which gives higher sensitivity at small currents. Also, an additional 10 kΩ resistor has been added to make the electroplating process more symmetrical. A typical trace of \(I_m\) vs. plating time is shown in Fig. 2b. In this particular case the gap has been closed to show the full behavior of \(I_m\). Low \(I_m\) on the left side corresponds to a large electrode separation. At the right side (high current), the electrodes are completely bridged with electrodeposited platinum. The curve contains step-like features. Scanning Electron Microscope (SEM) imaging on many sample samples suggest that they are caused by the granular Pt growth.

To calibrate the relation between monitor current and electrode separation we stop the electrodeposition process at different, predetermined values of \(I_m\). The electrodes are then removed from the solution, rinsed with de-ionized water and blown dry with nitrogen. After cleaning in an \(O_2\) plasma, samples are mounted in a Hitachi s-900 Scanning Electron Microscope which has a nominal resolution better than 1 nm. This allows a precise determination of the electrode separation. We find that to a given value of \(I_m\) corresponds to a well-determined value of the electrode separation, which is reproducible within \(\sim 10\%\). For the geometry and electrolyte discussed in this chapter we have fabricated and carefully inspected more than 20 electrode pairs: we find that \(I_m = 30\) nA corresponds to a separation of 16 nm, \(I_m = 90\) nA to 10 nm and \(I_m = 140\) nA to 3.5 nm.

This reproducible relation between \(I_m\) and the electrode separation, extending to separations as large as 20 nm, has not been reported in previous experiments and is one of the main results of this chapter. It demonstrates that electrochemical narrowing can be controlled and used to bridge the dimension scale accessible with e-beam lithography to the atomic scale. We believe that the ability to electrodeposイト Pt with very small grains is required to achieve the reproducibility and controllability reported here.

The behavior of the monitor current as a function of electrode separation is worth a comment. It has been speculated that the large current flowing between the electrodes at small separation is due to direct electron tunneling, enhanced by the presence of ions in the electrolyte. However, it seems unlikely that a
FIG. 3: SEM micrographs of three electrode pairs of different separation with individual Au clusters trapped in between them. From top to bottom, the cluster size is 20 nm, 10 nm and 5 nm. No cleaning prior to SEM imaging is possible without damaging the sample. This explains why the images of these samples are less sharp than those shown in Fig. 1.

A considerable contribution to the current can originate from direct tunneling for separations exceeding 20 nm. We presently do not understand the precise mechanism behind the increase of $I_m$ at small separation.

Pt electrodes with a few nanometer separation are remarkably robust. We have applied up to 5 V in air across electrodes separated by 3.5 nm, without observing any sign of degradation. This is in marked contrast with Au electrodes. For a comparable separation, Au electrodes normally break down when a few hundred millivolts bias is applied. This robustness makes Pt electrodes suitable to measure small nano-objects at high electric field. As an example, we have measured the electrical characteristics of individual Au nano-clusters of different dimensions (20 nm, 10 nm and 5 nm, commercially available from BBI international in mono-disperse solutions), electrostatically trapped (see Fig. 3). The room-temperature resistance of trapped clusters typically ranges between 100 MΩ and 10 GΩ, whereas the resistance across the electrodes before trapping is always larger than 100 GΩ, which is the limit of our measuring apparatus. These variations in the resistance can easily be explained by different geometrical contact configurations between the electrodes and the clusters, or by a different level of oxidation of the Pt surface.

Figure 4 shows $I-V$ curves measured at room temperature on a 5 nm cluster. It exhibits a pronounced non-linearity. The current suppression observed at low bias is consistent with Coulomb blockade through the cluster. The estimated self-capacitance of the cluster $C_0 = 0.27 \text{ aF}$ gives a charging energy of $E_C = 290 \text{ meV}$, which compares well to the size of the measured gap. To demonstrate the reproducibility of the measurements, two curves are shown in Fig. 4.

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