Nanometer-spaced 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 nanoclusters. 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. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1433914]

Modern chemistry has produced a large variety of objects perfectly defined on a molecular level that are of interest for the development of nanoscale 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 nanoobjects. 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 electron (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.[6,7] In this technique, metal electrodeposition on two planar electrodes (fabricated by conventional means) is used to reduce their separation. 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 interelectrode separation on a length scale larger than 1–2 nm and, if so, whether it is possible to calibrate this method with sufficient accuracy and reproducibility.

Here, we report a systematic study of nanoelectrode fabrication by means of electrochemical narrowing. We show that by optimizing the electrode layout and the control circuit we can monitor the interelectrode 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 nanoclusters 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 s which isotropically etches approximately 30 nm of SiO_2. 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

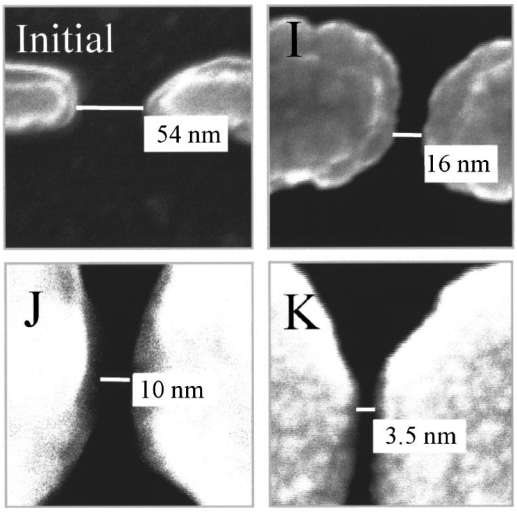

FIG. 1. Upper left corner: the initial separation of the electrodes as defined by electron beam lithography and lift-off is 60 nm. Figures I, J, and K show electrodes fabricated by stopping the electrodeposition process when the monitor current was 30, 90, and 140 nA, respectively. The electrode separations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

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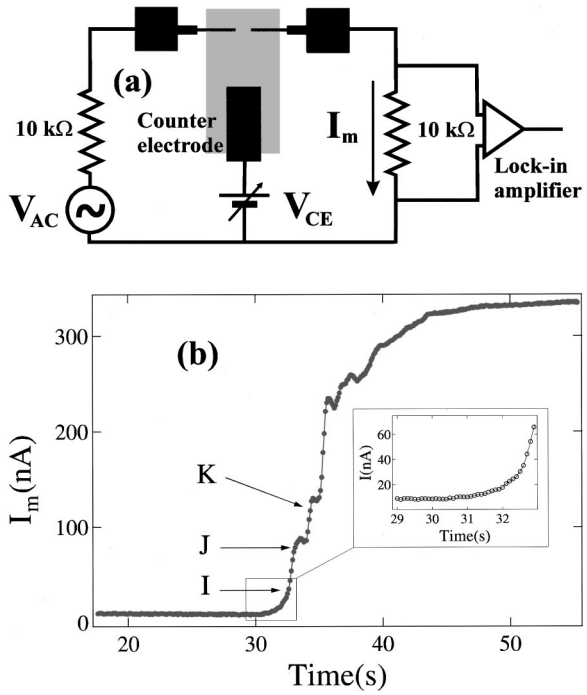

FIG. 2. (a) Circuit schematics to electrodeposit Pt and to monitor the electrode separation. During the electrodeposition process, the voltage applied to the counter electrode is $V_{CE}=420$ mV. The monitor current is measured in phase with the ac excitation using a lock-in amplifier ($V_{ac}=10$ mV, $f=10$ Hz). The shaded region represents the part of the circuit immersed in the electrolyte. (b) Monitor current vs time. A pronounced increase of I_m is observed as the electrode separation decreases (the inset shows the initial phase of this increase). At three predetermined values of the monitor current (pointed by the arrows) electrodeposition was stopped and the electrode distance measured using a SEM (see Fig. 1).

from the electrode extremities is also of importance. As compared to Ref. 6 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 mol of K_2PtCl_4 and 0.5 mol of H_2SO_4.[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 pretreatment of the electrodes. When following the same procedure with Pt, the material grows with a very rough morphology (i.e., grains of random size nucleate 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 O_2 plasma. We then put the electrodes in solution and apply a square wave signal. The voltage changes from -1.8 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 counterelectrode (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 interelectrode conductance during growth is done using a lock-in amplifier [see Fig. 2(a)]. 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 versus plating time is shown in Fig. 2(b). Low I_m on the left side corresponds to a large electrode separation. At the right side (high current) electrodes are completely bridged by electrodeposited platinum. 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 which has a nominal resolution better than 1 nm. This allows a precise determination of the electrode separation. We find that a given value of I_m corresponds to a well-determined value of the electrode separation, which is reproducible within ~10%.[9] For the geometry and electrolyte discussed in this letter 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–10 nm and $I_m=140$ nA–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 letter. 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 electrodeposit Pt with very small grains is required to achieve the reproducibility and controllability reported here.[10]

The behavior of the monitor current as a function of electrode separation is worth a comment. It has been speculated[6] 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 considerable contribution to the current can originate from direct tunneling for separations exceeding 20 nm. The precise mechanism behind the increase of I_m requires further investigations.

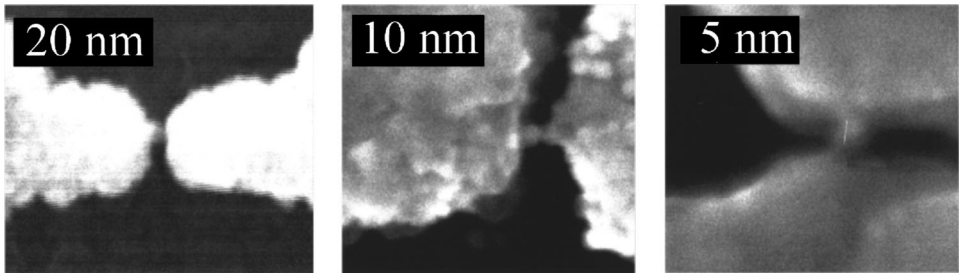

FIG. 3. SEM micrographs of three electrode pairs of different separation with individual Au clusters trapped in between them. From left to right the cluster size is 20, 10, and 5 nm. No cleaning prior to SEM imaging is possible without damaging the sample. This explains why the images of these samples are less sharp than those shown in Fig. 1.

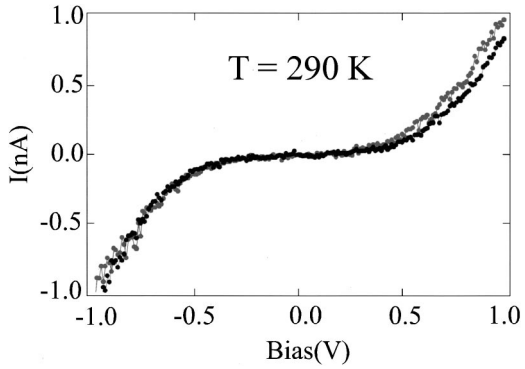

FIG. 4. Two room-temperature $I-V$ characteristics of a 5 nm cluster trapped between Pt electrodes, taken a few minutes after each other. The $I-V$ curves display a flat region of about 500 mV. This value corresponds well with the one expected from the theory of coulomb blockade ($2E_C=580$ meV).

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 nanoclusters of different dimensions (20, 10, and 5 nm, commercially available from BBI international in monodisperse solutions), electrostatically trapped[11] (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 nonlinearity. The current suppression observed at low bias is consistent with Coulomb blockade through the cluster. The estimated self-capacitance of the cluster $C_0=0.27$ aF gives a charging energy of $E_C=e^2/2C_0=290$ mV, 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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