

Cross beam lithography (FIB+EBL) and dip pen nanolithography for nanoparticle conductivity measurements

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Focused ion beam lithography is a very powerful technique for directly writing patterns on many substrates, it is a maskless and resistless technique that allows a very wide range of applications, providing a resolution down to 10 nm. Using a system composed by a 30 keV gallium ion beam column plus a 30 keV electron beam, nanogaps for electrical measurements of nanoparticle were fabricated with a resolution down to the nanometer scale, by exploiting FIB milling (FIBM) and electron beam lithography (EBL). Starting from prepatterned samples a square pattern reduces the width of the gold wire and a narrow line pattern opens a gap of less than 7 nm. Electrical measurements and AFM tapping mode imaging were performed on the gaps. We patterned the ends of the gold leads with dip pen nanolithography using mercapto-undecanol (MUD) to form a bond between the nanoparticle and the alcohol group attached to the gold surface. After this assembly, devices showed an increase in conductivity (10–100-fold increase). Measuring the device again one week later, we saw almost no change in conductivity, showing that we deposit a multiparticle cluster and measure its conductivity. © 2005 American Vacuum Society. [DOI: 10.1116/1.2062647]

I. INTRODUCTION

Focused-ion beams (FIB) have been widely used for high-resolution nanofabrication and microelectronics. FIB finds its use in various modes such as ion implantation, exposure of resist, ion milling, gas-assisted etching, and ion-assisted deposition of material.^{1–3} This versatility permits us to apply this technique in a wide range of applications where other techniques are not capable or are too difficult and complex. If we combine FIB with a SEM facility on the same platform, it is possible to realize several prototype devices in a simple and speedy way. In fact the possibility to fabricate in the nanometer region by the FIB and to align it as well as to inspect *in situ* with SEM, permits us to save a lot of time

optimizing all the process parameters. One of the most attractive applications of this hybrid approach is the realization of metallic electrodes with nanometer separation. These electrodes are ideally suited for electron-transport studies of chemically synthesized nanostructures and their possible applications.

This technology has recently attracted an increasing interest from scientific and engineering communities as a novel tool for electrical characterization of individual molecules⁴ and nanocrystals.⁵ Electron transport through these chemical nanostructures is strongly affected by electron-electron repulsion and energy level quantization, and transport experiments can provide detailed insight into the electron dynamics. Despite considerable progress during the last decade, however, the field of nanometer-scale electron transport is still in its infancy. One of the major obstacles impeding further progress is the lack of reliable methods to interface a

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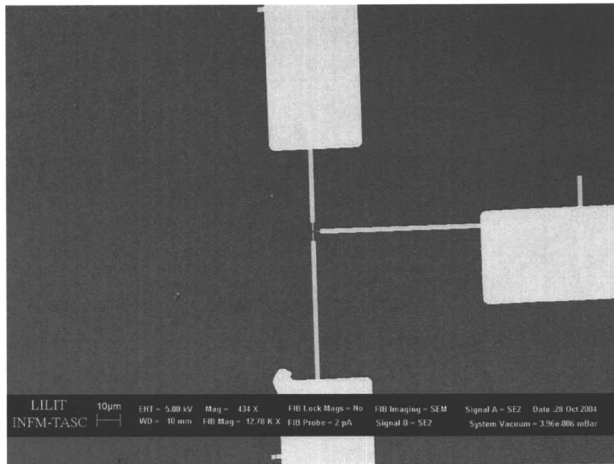


FIG. 1. SEM images of the gold pattern made by a combination of optical and e-beam lithography.

chemically-synthesized nanostructure to macroscopic electronic circuits. In its simplest realization, an electrical measurement requires the fabrication of metallic electrodes whose separation is comparable to the size of the nanostructure itself.^{6–8} The resolution limit of current lithographic techniques remains, however, on the order of 10 nm, and, consequently, the reproducible generation of the required electrodes is difficult by conventional fabrication techniques. The resolution obtainable by FIB (less than 7 nm) could present a good candidate for the fabrication of the electrode. Using DPN, it is possible to direct the assembly of nanoparticles with a high precision.⁹

One of the most promising techniques for directed assembly of nanostructures, DPN, was developed by Mirkin and co-workers as a versatile method to deposit molecules on various surfaces using the tip of an atomic force microscope (AFM) as a transfer tool.¹⁰ Since its discovery, many groups in the world have been successful in using DPN for writing molecules on metal and semiconductor surfaces.^{11–14} Applications of DPN include the fabrication of protein and DNA arrays, magnetic arrays, metal nanoparticle-based structures, and masks for the etching of nanosized gold features. Due to its enormous potential, DPN has attracted fundamental research on its enabling mechanism.

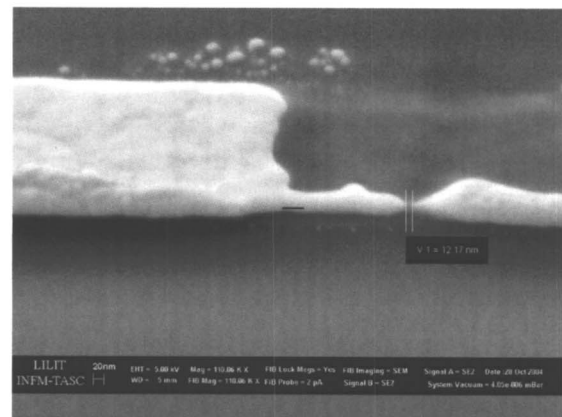
This paper presents a simple yet highly reproducible method to fabricate electrical circuits with nanogap by means of electron beam lithography (EBL) and FIB lithography. The control of the dimension (as measured by AFM) and the shape of the gap will also be demonstrated. Current versus voltage characteristics of the device are collected before and after the directed assembly of nanoparticles between gold leads chemically patterned using DPN. Measuring the device again one week later, almost no change in conductivity was observed, showing that we deposited a multiple Au nanoparticle cluster and measured its conductivity.

II. FABRICATION PROCESS

First, a pattern with large gold pads for the electrical contact was made using optical lithography and lift off process



(a)



(b)



(c)

FIG. 2. SEM images of pattern obtained using different FIB milling time; (a) gaps between 20 nm using 3 s, 10 nm (b) using 2 s and those with a thin gold wire branching the gap (c), using just 1 s. All 3 types of gaps were obtained with a good repeatability.

on a silicon dioxide substrate. The 200 nm wide Au wire connecting the two pads was patterned by EBL followed by evaporation and lift-off. The same pads were obtained using x-ray lithography at the LILIT beam line at ELETTRA synchrotron light source in Trieste with a single exposure.¹⁵ The final pattern is shown in Fig. 1 where the large Au pads are connected by a thin Au wire. Previous experiences had shown that the narrow gap should be between two extremely thin tips so individual particles can be addressed; wider wires

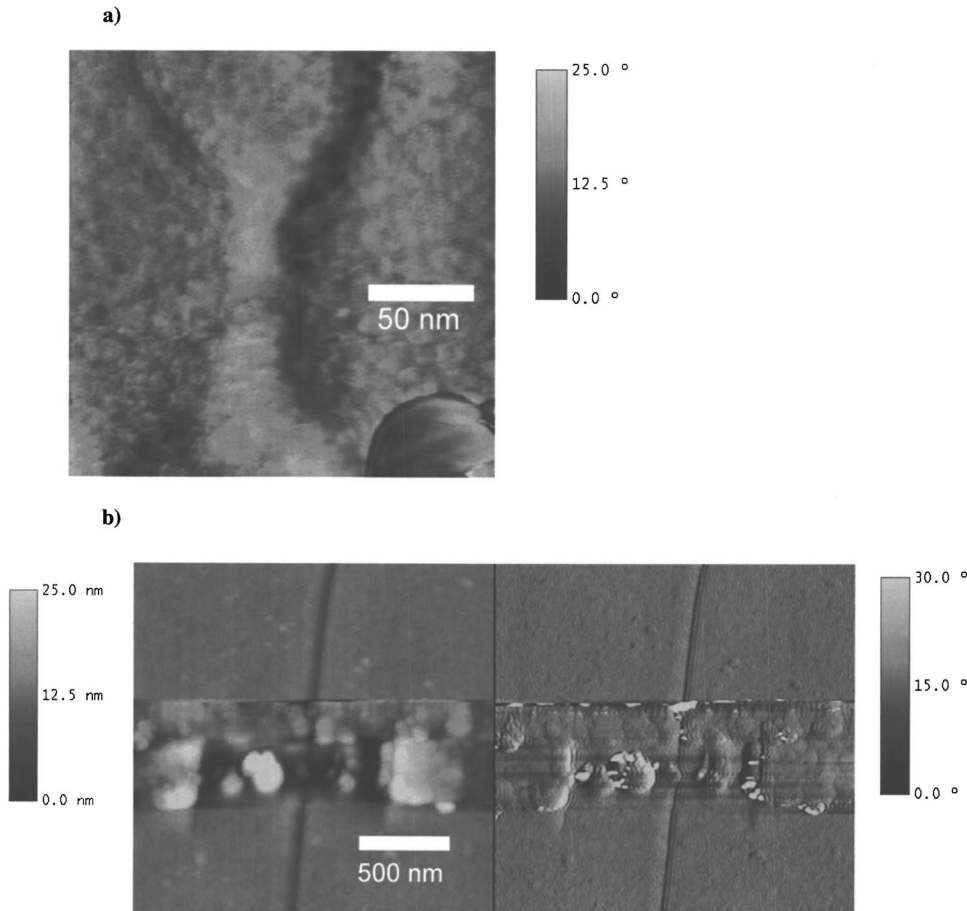


FIG. 3. (a) AFM image of the tips of the structure of Fig. 2(b) showing the narrow gap of about 10 nm. (b) AFM image (height and phase) of a smaller gap obtained from the samples of Fig. 2(c).

allow for millions of particles to be assembled in the gap, and electrical measurements will then only show the average properties of many particles. In the literature, it is possible to find examples of obtaining nanogaps by means of EBL, electromigration or using AFM to plow a gap.^{6–8} Using e-beam and lift-off process to pattern the gap of less than 10 nm could be quite difficult. Due to this consideration a different strategy was chosen. Using a dual-beam LEO XB1540 composed by a 30 keV/Gallium ion beam column plus a 30 keV electron beam GEMINI column, we have fabricated many devices with a resolution down to nanometer scale by exploiting FIB Milling (FIBM). The machine is powered by ELPHY RAITH lithographic software and pattern generator.

Using the stopping and range of ions in matter (SRIM) software it was possible to simulate the distribution and the implantation of gallium ions in the substrate. The presence of gallium ions is limited at few nanometer from the surface: around 7 nm for the longitudinal direction and only 5 nm for the lateral one. Such a small contamination does not affect the final result; the gold contacts remain good enough to be linked with nano particles compounds and the substrate maintains the insulation characteristics as shown by the electrical measurements.

The electron beam patterned gold wires were thinned by means of FIBM to reduce their dimensions to about 50–60 nm. The alignment was easily obtained by using the SEM capability of the machine; a prealigned coincidence

point between SEM and FIB permits the ion beam to act in the right position with a resolution of few nanometers. We use an ion current of 5 pA cutting a 1 micron square box in 10 s. The small gap on the thinned wire is obtained by a single line exposition 1 micron long for a time of 1–3 s. The different dose corresponds to a larger cut or a partial cut. In

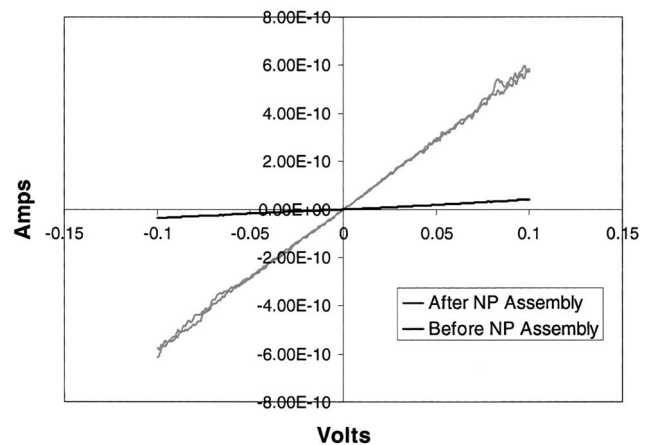


FIG. 4. *I-V* curves, showing a tenfold increase in conductivity (with respect to the conductivity of the preassembled gap) after assembly of 5 nm diameter Au nanoparticles coated with hexanethiol (HT) and MUD ligands and mixed with the di-isocyanate molecule; the particles were patterned with dip pen nanolithography. The curves were linear from -100 mV to 100 mV.

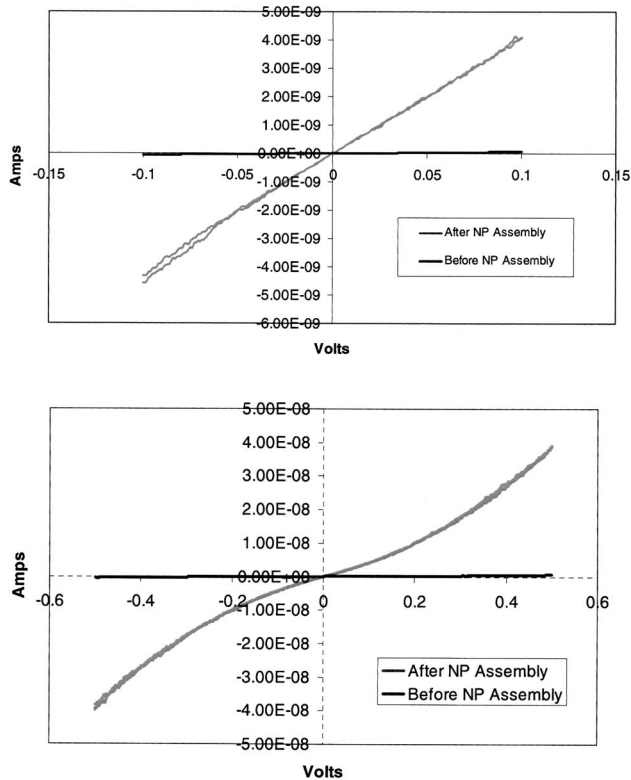


Fig. 5. After the assembly of a 5 nm diameter Au nanoparticle by DPN, this device showed a 100-fold increase in conductivity with respect to the pre-assembled gap; the curves shown were taken before and after nanoparticle deposition. Measuring the device again 1 week later, almost no change in conductivity was observed, demonstrating a strong, stable covalent bond.

Fig. 2 some SEM images of patterns are shown: they are obtained using different dose or (better) different exposure time; gaps between 20 nm, 10 nm, and even cuts that left a very small gold bridge branching the gap were obtained with a certain repeatability.

Figure 3(a) shows the AFM image of the tips of the structure of Fig. 2(b) showing the narrow gap of about 10 nm; Fig. 3(b) shows a tapping mode AFM image (height and phase) of a smaller gap obtained from the samples of Fig. 2(c) after the passage of current of few nA that break the residual wire via electromigration. In the AFM image, it is clearly visible that the FIB cut extended onto the SiO_2 substrate.

Electrical measurements on the gap showed a resistance of $4.0 \times 10^9 \Omega$ at 100 mV and $1.6 \times 10^9 \Omega$ at 1 V. Similar resistance values were measured in the other samples. This resistance is similar to values reported for sub 5 nm gaps.⁸

III. NANOPARTICLE ASSEMBLY

For all the FIB patterned samples the identical procedure was followed: taking electrical measurements, imaging with tapping mode AFM, DPNing mercaptoundecanol, assembling nanoparticles, and retaking electrical measurements.

The ends of the gold wires were patterned with DPN using MUD. The 5 nm diameter Au nanoparticles used in this experiment were coated with hexanethiol (HT) and MUD

ligands. The nanoparticles were then mixed with a diisocyanate molecule. The sample was immediately placed into this solution and allowed to sit overnight. The goal is to form a covalent bond between one isocyanate group and the alcohol group attached to the nanoparticle and a second covalent bond between the other isocyanate group and the alcohol group attached to the surface, covalently binding the nanoparticle to the end of the Au wire.

After NP deposition, contact mode pushes the nonspecifically bound nanoparticles on the surface. The covalently bound nanoparticles however cannot be moved.

IV. ELECTRICAL MEASUREMENTS AND COMMENTS

After assembling nanoparticles in the gap, electrical measurements (current versus voltage) were taken. Figure 4 shows a set of I versus V curves taken at different times; there was a ten fold increase in conductivity with respect to the open circuits; the curves were linear from -100 mV to 100 mV. Increasing the applied bias past 300 mV, caused a decrease in current with each successive measurement. It is believed that at this higher bias, an electromigration effect occurred breaking the thin wires at their weakest points.

A second device, the device shown in Fig. 3(b), was also patterned with MUD and exposed to the nanoparticle/diisocyanate solution overnight. This device showed a resistance of $2.5 \times 10^7 \Omega$ at 100 mV and $1.25 \times 10^7 \Omega$ at 500 mV (a 100-fold increase in conductivity, Fig. 5 shows the I - V measurements taken before and after nanoparticle deposition).

There was no Coulomb blockade present at room temperature, but there was definitely a change in slope around 200 mV, as shown in Fig. 5. The hypothesis is that we are measuring many nanoparticles at once, and as the bias is increased, more electrical channels through the nanoparticle clusters are made available for conduction.

V. CONCLUSION

In this paper a new technique for the fabrication of the nanogap was shown. Using a cross-beam system we could join the advantages of the FIB patterning (resistless, mask less, high resolution) with *in situ* SEM observation: easy alignment on a prepatterned sample, instantaneous diagnostic and correction. FIB milling permits us to modify a pre-existent pattern with a nanometric precision in the way to obtain a very sophisticated device. The total time for the fabrication of the single "gap" is approximately a few seconds and gives a immediate check of the results. This strategy permits the fabrication of a large number of devices that could be used for the particles deposition.

These nanogaps devices were used with DPN technique to deposit nanoparticles whose electrical properties could be measured.

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