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Controlled Deposition of Gold Nanowires on Semiconducting and Nonconducting Surfaces

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ABSTRACT

One of the pressing problems in advancing nanoelectronic applications and systems is to develop a simple means of freely connecting at a nanometric level electronic components under ambient conditions without the need for vacuum or electron or ion beam operational steps. Such environments may have detrimental effects on the molecular or biomolecular constituents of molecular electronic circuits. Although there has been defined progress in connecting structures that are of nanometric dimension, new methods in this area of nanotechnology with general applicability add to the arsenal of tools for addressing this standing problem. This paper addresses freely placing under ambient conditions, with fountain pen nanolithography, a 120 nm dimension line of gold nanocolloids deposited with precise registration in a 100 nm gap between two 250 nm wide conducting electrodes patterned by electron beam lithography.

The controlled deposition of metallic nanowires and nanoparticles has broad implications for a variety of areas. One of the most important areas for such selective deposition of nanowires is in molecular electronics, where a high degree of control for the deposited nanowires and nanoparticles would allow contacting molecules with potential for electronic applications.[1−3] Another area of importance is the deposition of nanowires and nanoparticles, where gold and silver nanostructures are being actively pursued for the guiding and switching of light in nanometric domains.[4,5] A third area of importance is the deposition of arrays of nanoparticles for possible sensor applications.[6,7] For all of these reasons, there have been numerous studies aimed at developing techniques for such controlled deposition of metallic particles and nanostructures on a variety of substrates.

Among these techniques, are the developments in the methodologies of what has become known as dip pen lithography (DPN) that has been pioneered by Mirkin and co-workers.[8,9] The DPN technique was originally designed to work on gold surfaces where ambient water layers produce diffusive transport of a set of inks. Metallic surfaces, however, are not ideal for many of the electronic, photonic, and sensing applications mentioned above. As a result, there have been a whole set of defined studies with DPN and with other AFM-based methods to deposit metal nanoparticles as dots of clusters or lines on a variety of substrates. These include deposition on silica[10] through diffusive transport of dried clusters of nanoparticles on an atomic force microscopy (AFM) probe; nanoscratching with nanobrushing of metallic particles on metallic surfaces;[11] electrochemical deposition of Au^{3+} on a semiconductor surface such as silicon;[12] and spontaneous formation of ordered gold and silver nanoparticle stripe patterns on dewetting a dilute film of polymer.[13] In addition, an ingenious technique has been developed using thermally activated decomposition of an organic monolayer with a laser beam.[14] This technique leaves a fine line of organic monolayer by the use of the interplay of a laser induced temperature rise and the thermal decomposition of organic material. Remarkably, this method has allowed for lines as small as 100 nm to remain on the surface using specific organic materials. Furthermore, lift-off technology with electron beam lithography has been employed to make plasmonic structures of gold and silver in a multistep process.[4] Finally, electron or ion beam deposition of a variety of gases has been employed for the production of nanowires and other structures, but these methods require an evacuated environment[15] that could be damaging for organic or bioorganic molecules, where water is critical to functionality and where there is a need to contact nanowires. In this paper, we demonstrate a method that can deposit gold colloid lines on a variety of substrates including such nonconducting or semiconducting substrates such as glass or silicon, respectively.

Our method is based on a technique called fountain pen nanolithography (FPN).[16,17] FPN uses a cantilevered nanopipette that had been shown earlier to be effective as an

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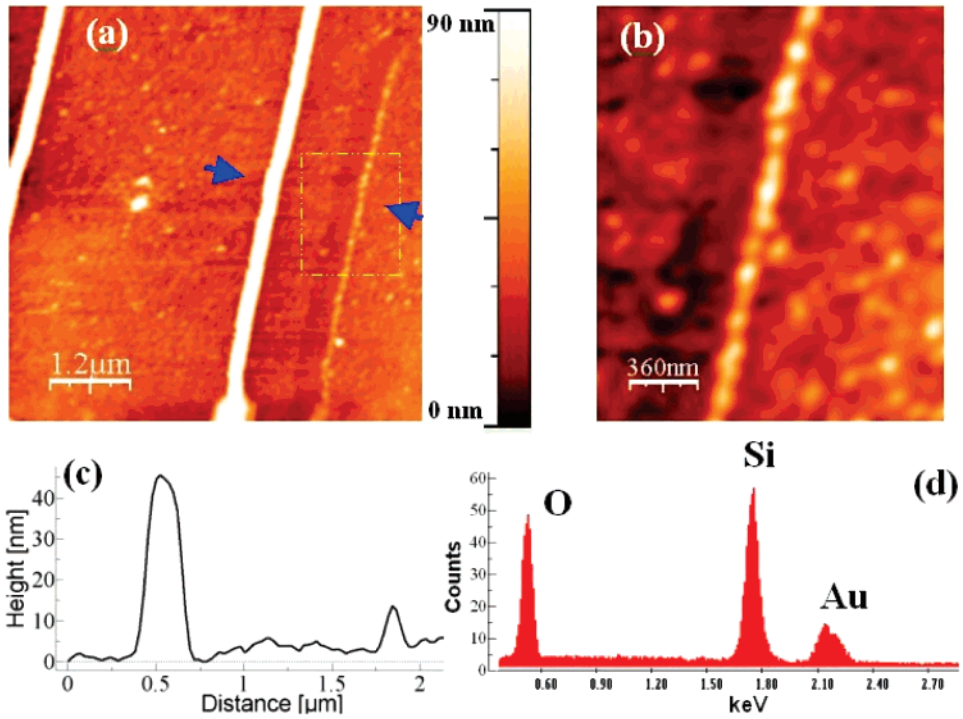

Figure 1. Gold nanoparticles line printed on semiconductor surface by FPN technique in close juxtaposition to a gold line produced by electron beam lithography technique. (a) AFM image shows the lines produced by electron beam lithography and the gold colloid line deposited by FPN on the right side of the image. Scale bar is 1.2 μm. (b) Zoom-in image of the marked area on (a) highlights the deposited line. Scale bar is 360 nm. (c) Height profile line between the marked arrows on (a) shows one of the electron beam lithography lines with width of 250 nm and height of 45 nm and the FPN deposited line with width of 100 nm and height of 15 nm. (d) Electron induced X-ray fluorescence spectrum of the FPN deposited line shows Au on the right peak.

atomic force sensor.[18] With such cantilevered nanopipettes, it is possible to flow both liquids and gases onto a surface with the nanometric control of normal force atomic force microscopy.[19] There are also studies in which the FPN method with cantilevered nanopipettes has been used to affect enzymatic reactions on protein substrates.[20] There are other investigations in which attempts have been made to emulate the cantilevered nanopipette structure in silicon for nanowriting.[21,22]

The attractive characteristics of nanopipettes for chemical delivery on the nanoscale have also led to attempts to use straight rather than cantilevered nanopipettes. Such straight nanopipettes lack normal force sensing. Two approaches have been used to contend with this limitation. One has been to use a method of shear force that has been used previously in near-field microscopic applications.[23] A second approach around this limitation is to write within a liquid and to use the conductance through the nanopipette as a feedback mechanism.[24]

To harness nanopipette delivery for printing conducting nanowires on nonconducting or semiconducting surfaces in a generally applicable way, FPN with the control of normal force sensing is combined with suspensions of gold nanocolloids as the ink. To demonstrate the relative capability of this method, we have used a semiconductor surface on which nanoelectrodes have already been produced by standard 0.25 μm electron beam lithography techniques. This allowed us to compare the nanowires printed by FPN on a semiconductor surface with features produced by standard microelectronic fabrications methodologies.[25] In addition, we were able to affect a task of importance in nanoelectronics in general, i.e., to freely write a conducting line in registration with another conducting structure on a semiconducting surface

For the writing operation, we use 1.2 nm gold nanoparticles with an attached amino group suspended in methanol.[26] The methanol suspension (0.1 nmol/mL) was loaded into the nanopipette nanofountain pen and, when encapsulated in a nanopipette, the suspension was stable for up to 1 h without significant evaporation. The nanopipette is fed with the methanol/gold suspension from the large end of the pipette, and capillary action readily drives the solution to the tip of the cantilevered nanopipette. When the nanofountain pen touches such a surface, the gold particles in the methanol flow out of the tip and the methanol rapidly evaporates, leaving a line of the metallic particles. An example of such a line printed by a nanopipette with a 100 nm tip-opening and a writing speed of 0.1 μm/s, in close juxtaposition to a gold line produced by electron beam lithography, is shown in Figure 1. By using AFM, we can show that this line (on the far right of the image) is 100 nm wide and ~15 nm high. This is to be compared to the lines produced by electron beam lithography, which are measured to be 250 nm wide and 45 nm high.

The fidelity of the writing in terms of line continuity, line height, and line width is related to different parameters such as the probe diameter, the set points used, the concentration of the suspension, and the hydrophobicity or hydrophilicity of the surface. For example, the probes that were used in

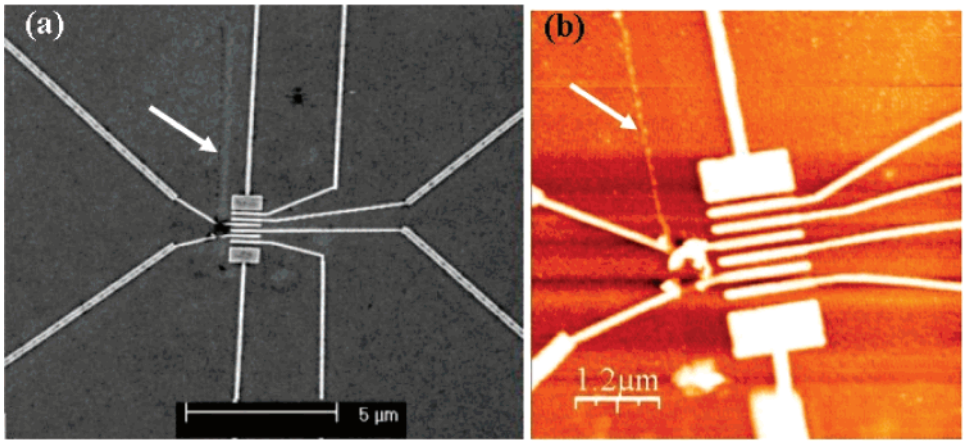

Figure 2. SEM and AFM gold nanoparticles line printed on semiconductor surface. (a) SEM image shows the gold nanoparticles line printed by FPN. Scale bar is 5 μm. (b) AFM image of smaller area than in (a) shows the same printed line as in (a). The deformed part in the center of the image demonstrates that if a set point is chosen that is higher than approximately 20% of the maximum then, due to the high force constant of the cantilever, the surface can be scratched. Scale bar is 1.2 μm.

the writing on a silicon surface had a force constant of 10 N/m, and were used in contact mode. They had a tip aperture of 150 nm, and were filled with the colloid suspension with a concentration of 0.1 nmol/mL. For such a solution and these probes at a set point, which was approximately 10−20% of the maximum set point of the system,[27] speeds of writing from 1 μm/s to 50 μm/s resulted in line widths from 1 μm to under 100 nm, respectively. Under these conditions, the height of the line varied from 100 to 10 nm.[19] All AFM imaging and FPN writing were done with a Nanonics MultiView 1000 system (Nanonics Imaging Ltd, Jerusalem, Israel).

To verify that gold has been deposited onto the silicon surface, the gold line written in Figure 1 was probed using electron induced X-ray fluorescence. The results obtained are shown in Figure 1d. The gold is clearly detected in this spectrum, giving us confidence that the line printed is indeed composed of gold particles.

We suggest that a plausible mechanism that accounts for the gold particles associating with the silicon surface involves the amino group on each particle. The isolelectric point of such a silicon oxide surface is between 1.8 and 2.7.[28,29] This would mean that, under the conditions of our deposition, the surface would be negatively charged and would evidence favorable Columbic interactions with the positively charged ammonium groups attached to the gold particles.

To further test the conductivity of the nanowire over and above the EDX measurement, a scanning electron microscope image of the printed line was obtained within the context of the larger structure in which it was printed. SEM and AFM images are shown in parts a and b of Figure 2, respectively. The gold nanoparticles deposited line was printed using the same parameters as for Figure 1 but with higher setpoint. The fact that the line was seen clearly in the SEM image gave us another indication that such lines may be conducting because electron beam techniques can only effectively image conducting structures.

To further investigate the conductivity of such gold nanowires, we wrote such a wire across a 100 nm space between two gold lines that had been produced by electron beam lithography. These gold lines were connected to larger pads, as in Figure 3a, and the pads could be effectively contacted to investigate the conductivity of our printed gold lines. In Figure 3a, we show an optical image of the patterned structure produced by electron beam lithography. An optical image with higher magnification of the inner electrodes is shown in Figure 3b. The nanopipette probe with an aperture of 100 nm was fed with the methanol/gold suspension, and using the same set of parameters as in Figure 1, a line of gold colloids was written with registration across the gap, as displayed in the AFM image of Figure 3c. The profile of the line in (c) along the dashed line is displayed in Figure 3d, demonstrating a line width of 120 nm and height of 30 nm. The electrical behavior detected for this nanowire is also shown in Figure 3e, where a current−voltage ($I-V$) plot was measured between the two electrodes by using a standard probe station connected to the larger pads that are seen in Figure 3a. The $I-V$ characterization demonstrates an Ohmic behavior with a resistance of ~4000 Ω.

Although the bulk resistivity of gold would predict a higher conductance, it should be noted that the line was made up of individual gold nanoparticles that were simply aggregated. The resistivity of our nanowire is low relative to the bulk resistivity of gold but high relative to the mega-Ohm resistances that were measured in a previous study on aggregated gold colloids in a metallic gap.[30] The higher conductivity of our aggregated gold nanocolloids structures probably results from the relative size of the gold colloids used in our study. We used 1.2 nm gold colloids, whereas the previous study used gold nanocolloids with diameters of 40−100 nm. The ultrasmall dimensions of our nanocolloids probably result in more effective aggregation, which accounts for the higher conductivity. Also, it should be noted that $I-V$ curves of printed electrodes with similar gaps but without gold nanoparticles had a huge resistance of hundreds of mega-Ohms. In summary, the resistivity of our nanowires, although still needing improvement relative to resistances that are obtained with focused ion beam deposited metallic

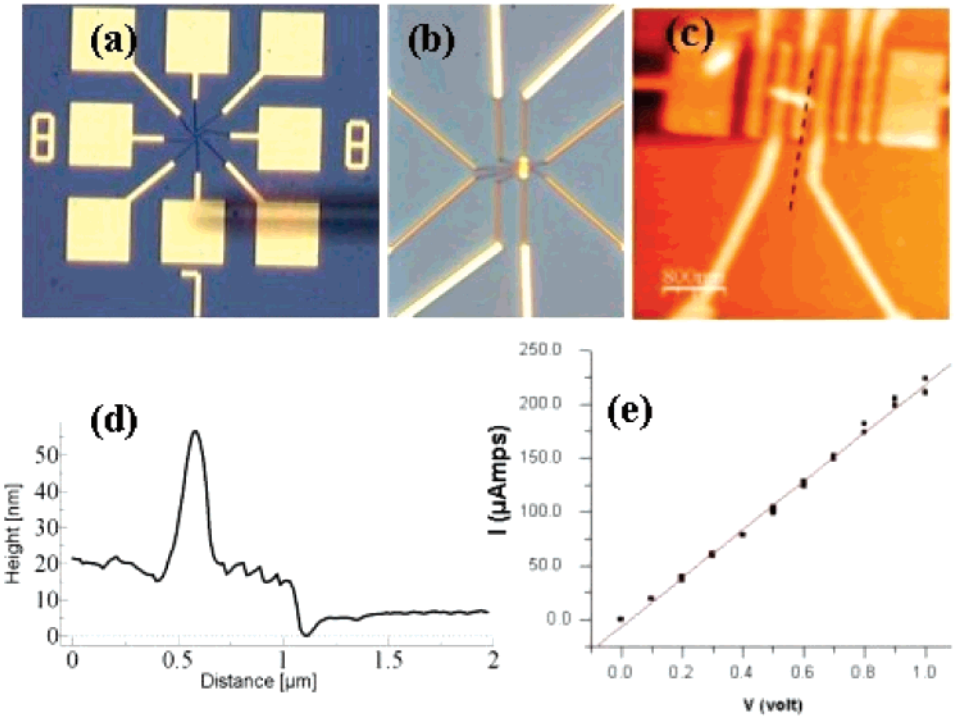

Figure 3. FPN Gold colloids line deposited in the interconnection of a 100 nm separation of two conducting wires for current−voltage characterization. (a) Optical image shows the inner electrodes pattern for the $I-V$ characterization (×100 magnification). (b) Optical image of the inner electrodes area (×1000 magnification). (c) AFM image shows the inner electrodes pattern with a printed gold nanoparticles wire crossing a space of 100 nm between two electrodes. (Scale bar is 800 nm). (d) Height line profile of the dashed line on (c) shows the gold nanoparticles 120 nm line on top of one electrode. (e) $I-V$ characterization of the printed line shows an Ohmic behavior with resistance of ~4000 Ω (y-axis in units of microamps).

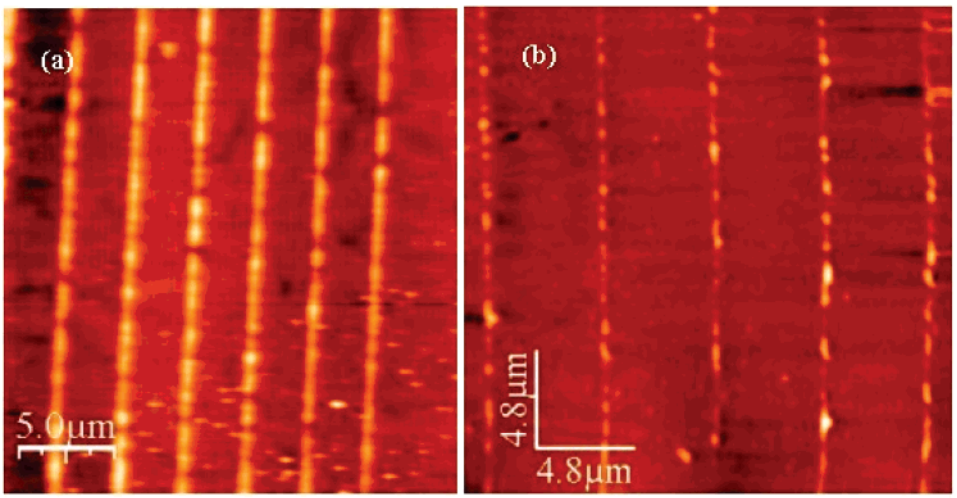

Figure 4. Gold nanowires printed by FPN on a modified aldehyde glass substrate with different pipet apertures. (a) Gold nanowires array with average width of 550 and 60 nm average height printed by a pipet with aperture opening of 200 nm (scale bar is 5 μm). (b) Gold nanowires array with average width of 350 and 30 nm average height printed by 100 nm aperture pipet (scale bar is 4.8 μm).

lines (150 times less than bulk gold), shows a significant advance over previously published results. One way in which to improve the conductivity of our lines would be to introduce a heating cell into our scanned probe microscope, which could then be used to anneal the gold particles effectively.

We have also shown that other types of chemistry can be used with such amino gold suspensions to write gold wires whose dimensions can be varied depending on the size of the nanopipette opening, writing speed, and applied pressure on the AFM nanopipette probe. As an example of such gold wires, we have used surfaces functionalized with aldehyde groups; these surface are commercially available and are called Superaldehyde glass surfaces.[31] The interaction of the methanol suspensions of the amino gold with such surfaces forms a Schiff base linkage that permits effective immobilization of the gold lines. Shown in Figure 4 are lines written with 100 and 200 nm pipettes, and the gold wires

that were printed have dimensions of 350 and 550 nm, respectively. Contact mode with a 10% setpoint of the maximum setpoint of the system and a writing speed of 5 μm/s has been used. The line width, height, and continuity can be improved by optimizing the writing parameters. These structures show that the same technique can be used for writing lines with a variety of widths as the problem at hand dictates.

It should be noted that this method of fountain pen deposition probably can be interfaced effectively with many different types of surfaces and with many different types of nanoparticles. In essence, a variety of chemical parameters can be controlled both in terms of the particle, the surface, and the probe. An example of another family of nanoparticles is TiO_2 in aqueous suspension, and this was investigated by Taha[19] on highly hydrophobic and hydrophilic surfaces. On these surfaces, which were phenylether self-assembled monolayers that could be converted with sulfonation to a hydrophilic surface, the nature of the writing completely changed from repulsive to attractive interactions.

In summary, we have presented in this paper a simple method for depositing nanowires composed of ultrasmall gold colloids from a methanol suspension. The conductivity of these nanowires has been verified using three different methodologies, first, by measuring the current voltage characteristics of the line. This showed that such colloid-based lines had defined but low conductivity probably due to the colloidal nature of the particles and the lack of annealing. The extent of conductivity was in fact sufficient to allow the imaging of the line in a scanning electron microscope, which requires such conductivity for good image contrast. All these results were consistent with the EDX data, which showed that gold had in fact been deposited. The technique could in principle be quite useful relative to the variety of techniques that exist today for deposition of metallic lines. Specifically, its primary advantage is that such deposition can freely place these nanowires under ambient conditions with a technology that has in principle the capability of imaging the nanostructures onto which the wires should be placed. Nonetheless, one important improvement needs to be made in order for this methodology to be generally useful. Specifically, more control of the deposition process is required so that the column of the depositing liquid is effectively controlled relative to the interaction of the tip with the surface. Future work will be aimed in this direction, and the prospects of addressing this problem effectively are bright.

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