Nanotrench for nano and microparticle electrical interconnects

J-F Dayen, V Faramarzi[1], M Pauly[2], N T Kemp[1], M Barbero[1], B P Pichon[2], H Majjad[1], S Begin-Colin[2] and B Doudin[1]

1 IPCMS—Department of Magnetic Objects on the Nanoscale, 23 rue du Loess BP 43, F-67034, Strasbourg Cedex 2, France
2 IPCMS—Department of Chemistry of InorganicMaterials, 23 rue du Loess BP 43, F-67034, Strasbourg Cedex 2, France

Abstract

We present a simple and versatile patterning procedure for the reliable and reproducible fabrication of high aspect ratio (10^4) electrical interconnects that have separation distances down to 20 nm and lengths of several hundreds of microns. The process uses standard optical lithography techniques and allows parallel processing of many junctions, making it easily scalable and industrially relevant. We demonstrate the suitability of these nanotrenches as electrical interconnects for addressing micro and nanoparticles by realizing several circuits with integrated species. Furthermore, low impedance metal–metal low contacts are shown to be obtained when trapping a single metal-coated microsphere in the gap, emphasizing the intrinsic good electrical conductivity of the interconnects, even though a wet process is used. Highly resistive magnetite-based nanoparticles networks also demonstrate the advantage of the high aspect ratio of the nanotrenches for providing access to electrical properties of highly resistive materials, with leakage current levels below 1 pA.

1. Introduction

New breakthroughs envisioned for molecular and nanoelectronics in the area of information storage and processing [1, 2] have motivated a significant boost to both fundamental and applied research in the area. Electronic transport through nanoscale entities, down to a single molecule [3–7], can potentially take advantage of exciting multi-functional properties, with the expectation of dominant quantum mechanical effects. It has become increasingly clear that the realization of robust single molecule or single nanoparticle devices exhibiting reliable properties is a very challenging experimental task. The high sensitivity to chemical and electromagnetic environment [8, 9], and the modification of electrical properties due to local atomic arrangements or structural defects [10, 11], severely limit the stability and reproducibility of the experiments. Moreover, controlled unambiguous positioning of a molecular-sized entity in an electronic circuitry remains an open problem for scaling up industrial production. The development of single molecule based electronic devices for industrial purposes seems therefore premature at this time.

A possible route to reconcile the molecular scale (below 1 nm) and the top-down nanofabrication route (larger than 10 nm) is to use a multi-scale approach, where a cluster (metallic, semi metallic or semiconductor) of typical 10 nm size [12] or a conducting

microsphere, of typical 10^2–10^3 nm size, are used as an intermediate bridge. One can also take advantage of bottom-up fabrication methods for incorporating macroscopic amounts of identical molecules into devices, or to assemble well organized monolayers of nanoparticles [13–15]. Key advantages are simplicity, ability to cover large areas, and cheap manufacturing costs. Large numbers of interconnected molecules also ensure device robustness through ensemble averaging [16, 17]. Nanoscale entities such as functional ordered arrays of nanoparticles also represent an alternative opportunity for designing new devices such as gas sensors, electro-optic devices or magneto-electronic nanodevices [18–20]. The transport and magneto-transport mechanisms taking place are often very sensitive to electrode/nanoparticle molecular interface, which can create artifacts or difficulties in unambiguous interpretation of the data. Devices based on multiple connected nanoparticles should be less sensitive to such artifacts and improve the reproducibility of the measurements from one sample to the other. Hence, there is a need for a versatile configuration of device, compatible with bottom-up fabrication methods, and made by standard optical lithography techniques to keep manufacturing costs down.

A planar electrode geometry, directly inspired by top-down nanofabrication techniques, provides several key advantages. First, the integration of a three terminal configuration device capable of gating the flow of carriers can be easily implemented. Then, planar substrates are also ideally compatible with bottom-up fabrication methods of nanoparticle layers such as Langmuir related techniques. Finally, the open direct access to the middle molecules or nanoparticle layer optimizes chemical and optical control or excitation. This is particularly attractive if we want to gain access to the intrinsic properties of the molecules, with the prospect of realizing multi-functional devices. Lateral geometry also provides unique advantages versus the more ubiquitous vertical geometry [21–23], where metal electrodes sandwich an organic film. Such a geometry suffers from the key problem of possible formation of leaking metallic paths during the deposition of the top electrode [24, 25], which can only be avoided by adding an intermediate highly conductive polymer film [16].

We propose to design wide electrodes (up to 100 µm), separated by a short distance (down to 20 nm) corresponding to the typical thickness in organic vertical structures. There is an extensive literature on nanofabrication techniques for realizing close electrodes, and it is clear that such size should be easily reachable by e-beam lithography tools. One should however emphasize that the critical issue of obtaining high aspect ratio (HAR) gaps below 50 nm is an extremely challenging task, necessitating state-of-the-art electron beam equipment, which might suffer from reliability issues when extremely high aspect ratios are desired. More importantly, the use of a sacrificial layer becomes necessary if aspect ratios exceeding 10–100 are needed. Layers made of aluminum oxide [26], chromium oxide [27], or molecular monolayers [30] are reported in the literature. All these techniques suffer from the necessary etching process, which needs to be critically selective and critically efficient.

Realizing HAR gaps devices become critically important when materials with intrinsically large resistivity are investigated. In the field of nanoelectronics, materials with sheet resistances of high value are commonly encountered. Hopping transport makes low temperatures measurements critical and becomes a practical limitation to studies. Oppositely, when low resistance samples are investigated, series resistance of the leads, and their intrinsic resistivity, might limit the measurement quality and reliability. There is therefore a need for realizing planar electrode interconnects with a large HAR that exhibit good interface resistance. We are not aware of reports of patterned circuits with unambiguous examples of adequacy for both low and high impedance system investigations.

One industrially attractive approach that does not rely on electron beam lithography, maximizes the reliability for HAR trenches, and minimizes contamination, is the so-called shadow evaporation method [34]. This technique has been used previously to make nanogaps of very small width (around 100 nm) to contact single entities [31, 32], or to make templates for nanowire and nanochannel patterning. [34, 35] We report the successful and reproducible fabrication by a standard optical lithographic process of HAR gap devices made of two planar electrodes separated by a 'nanotrench' 20–100 nm wide and up to 100 µm in length, i,e. a ratio up to 5×10^3. This ratio can be straightforwardly increased by 1–2 orders of magnitudes by using an inter-digitized geometry. Avoiding the use of more sophisticated lithography techniques makes our fabrication strategy more relevant for industrial scaling up. Reports of a similar approach for fabricating long channels or wires can be found in the literature, using the nanotrenches as a mold and mostly aiming at biological applications. However, unambiguous indication of the quality of the realized gaps over the whole length of the trench cannot rely on imaging methods only.

Our goal is to provide compelling evidence of the adequacy of the shadow evaporation approach for making trenches with no detrimental structural defects for applications in electronics. We demonstrate the interest and reliability of this approach by presenting two examples of applications for nanoparticle and microparticle electrical properties, showing that no leakage or shorts are present in our structures, and that the electrical contacts are of good quality and suitable for a wide range of current measurements.

2. Experimental details

2.1. Fabrication of the electrodes

Edge mediated shadow mask lithography allows sample fabrication in two lithographic steps only. Micrometer-scale electrodes (figure 1(a)) are made of a Ti/Au bilayer (with typically 3 nm of Ti and 40 nm of Au) deposited using electron beam evaporation followed by a standard lift-off process. The first layer is patterned on silicon substrates covered with thermal oxide by 3.6 s of exposure through a positive mask over AZ5214 photoresist followed by 35 s flood exposure for image reversal. AZ726 MIF is used as a developer. After metal deposition, the lift-off process is performed in acetone. The second layer is made of lines crossing perpendicularly the first layer electrodes (figure 1(b)). Angle deposition (for example 65° for a gap of 80 nm) of the metallic Ti/Au bilayer is performed in a chamber with a large distance separating source and target (figure 1(c)).

Figure 1.

2.2. Nanoparticle synthesis

Iron oxide nanoparticles are used as a model system for potentially highly resistive materials. The iron oxide nanoparticles are obtained by thermal decomposition of an iron stearate precursor in a high boiling solvent. 1.38 g (2.2×10^{-3} mol) of Fe(stearate)$_2$ (99%, Strem Chemicals) and 1.24 g (4.4×10^{-3} mol) of oleic acid (99%, Alfa-Aesar) added to 20 ml octyl ether (99%, Sigma-Aldrich, b.p. 287 °C) [15]. The mixture is heated to 100 °C and stirred at this temperature to dissolve the reactants. The solution is then heated to 287 °C at a rate of

$5\,°C\ min^{-1}$ without stirring and refluxed for 120 min under air. The resultant black solution is cooled down to room temperature. The nanocrystals are then washed three times by addition of ethanol and centrifugation (8000 rpm, 10 min). A size selection procedure is applied by Size Selective Precipitation (SSP): the nanoparticles are suspended in hexane at a concentration of $1\ mg\ ml^{-1}$ and precipitated using the same volume of acetone. After centrifugation, the precipitate is collected and redispersed in THF. The SSP reduces the size polydispersity from 15% to 9%. The suspension is finally dialyzed for three days in THF in a 25 kDa regenerated cellulose membrane (SpectrumLabs) in order to remove any impurities or oleic acid molecule excess possibly still present after the first purification step. The nanocrystals covered with oleic acid can be easily suspended in various organic solvents (chloroform, toluene, hexane, dichloromethane).

2.3. Langmuir–Blodgett film preparation

A small volume (150 µl) of a $5\ mg\ ml^{-1}$ iron oxide nanoparticles suspension in chloroform is spread on the water subphase of the Langmuir trough (KSV 5000, 576 mm × 150 mm) at room temperature. The area available to nanoparticles is reduced by compressing the barriers (compression rate: 5 mm = min), and the surface pressure–area isotherm is recorded during the film compression using a Wilhelmy plate. Multilayer films are transferred from the water subphase to the substrate supporting the electrodes at a pressure of $30\ mN\ m^{-1}$ by pulling the substrate several times out of the water subphase at a rate of $1\ mm\ min^{-1}$.

2.4. Microsphere preparation

Polybead® Monodisperse Microspheres, with a 1.00 µm mean diameter (Polysciences), are diluted and washed in distilled water by centrifuging steps. After standard organic acetone/ethanol cleaning, followed by N_2 drying, the glass surface is made hydrophilic using oxygen plasma. The microspheres in solution are then spread onto the hydrophilic surface and dispersed uniformly after solvent evaporation. These substrates are covered by e-beam evaporation of 40 nm thick gold films deposited over 3 nm of titanium (as an adhesion layer). The spheres are then detached from the surface by sonication in ethanol, washed, collected by centrifuging, dispersed in ethanol, and then spread on the nanotrenches for bridging the electrodes.

2.5. Electrical measurements

 Electrical measurements are carried inside a vacuum-pumped cryostat ($P < 10^{-6}$ mbar) that can reach liquid helium temperature. Measurements of the DC electrical properties are performed using a semiconductor parameter analyzer (Agilent E5270B). Room temperature measurements are performed on a probe station with a four probe configuration (Karl Suss PM8).

3. Results and discussion

In the approximation of a collimated source, the shadowing results in a gap of size $G = \frac{h}{\tan(\theta)}$, determined by the evaporation angle θ and the height h of the first electrode layer (figure 1(d)). It is important to highlight that during the second lithographic step, the nanotrench area is not exposed to reticulated resist. This is of critical importance if molecular

electronic studies are envisioned, as possible residue from the reticulated resist after lift-off could interfere with the molecular signature under study or behave as small current leakage path.

The simplicity of the geometrical effect used in this process allows us to realize nanotrenches that are reproducible, uniform all along the micrometric length of the gap, and without resist contamination into the gap area. Gaps down to 20 nm on several micrometers length (figure 2(c)) are reproducibly obtained, locally reaching distances of the order of 10 nm. We routinely made several tens of samples with gap sizes below 100 nm and lengths ranging from 2 to 100 µm (see figure 2 for examples of HAR gaps of different length). These nanotrenches devices were obtained successfully on oxidized silicon wafers and on glass or quartz substrates compatible with optoelectronic measurements. Leakage currents below 1 pA for an applied bias up to 1 V are systematically found (figure 3(c)), and considered as benchmark values for high-electrical quality samples. Trenches of gap values down to the grain size of the deposited material, i.e. 10 nm, can be realized. But we observed a poorer reliability, as the majority of the samples with aspect ratios larger than 10^3 exhibit leakage currents in the nA range. Such borderline samples are therefore not considered, but reveal that critical assessment is provided by basic electrical characterization.

Figure 2.

Figure 3.

In the first example of a device, monolayer and multilayer films of iron oxide nanoparticles are deposited by the Langmuir–Blodgett method over the trenches. Films of magnetite-based NPs exhibit very interesting magneto-resistance values when compared to conventional films elaborated by physical methods and can potentially lead to the development of devices with enhanced magneto-transport properties [23, 28, 18]. In this study, we use magnetite-based NPs made of a conductive magnetite core and an oxidized shell, which provides intrinsic high resistance, to demonstrate the adequacy of the nanotrench pattern for measurements on intrinsically poorly conducting systems.

The iron oxide nanoparticles have an average size of 11 nm. The nanotrench is oriented along the axis of pulling during the deposition process. SEM images of monolayers and multilayers of iron nanoparticles successfully deposited into the gap are presented in figures 3(a) and (b) respectively. Once the magnetite film is assembled, oxygen plasma exposure is used to improve the electrical contact between the NPs. The resistance R decreases dramatically from the $T\Omega$ range corresponding to the empty nanotrench, to a value of a few $M\Omega$ (figure 3(c)–(e)), of magnitude comparable to previous results obtained on samples in the vertical geometry [23]. The observed dramatic current increases provides an immediate indication of the occurrence of a conductive path through the sample. The stability and the reproducibility of this observation confirm that the planar geometry is well suited for compatibility with wet chemistry film deposition processes such as Langmuir–Blodgett techniques.

We checked the stability of the electrical contact by cooling the sample down to 50 K. The resistance exhibits an exponential increase with decreasing temperature, well described by the

law $R \propto \exp(T^{-0.5})$ (figure 3(d)). Such a non-Arrhenius law has been previously reported [37] and is a signature of activated transport through the nanoparticle ensemble [33, 36]. Several reasons can be invoked to explain the dependency $R \propto \exp(T^{-0.5})$ (see review article [33] and references therein). One of the most likely explanations is that the nanoparticle assembly behaves as a network of resistors in the presence of electron–electron interactions, with structural and charge disorders due to a distribution in the interparticle distances and/or diameters [33, 36]. The interparticle distance distribution is confirmed experimentally by SEM pictures on figures 3(a) and (b), and might come from non homogeneous Langmuir–Blodgett deposition due to hydrophobic repulsion at the air–water interface. One should emphasize that the data at liquid He_4 temperature is expected to be in the 10 pA range, making the use of a vertical geometry [23] or HAR gaps design critical for characterizing the samples at low temperatures.

The second example of device is made of a microsphere, partially coated with Au, and trapped between the two electrodes. Such an approach has been proposed recently for studying molecular junctions, where metal-coated micron-size spheres were covered with a molecular film and magnetically trapped between electrodes patterned by e-beam lithography [29]. Here we present complementary experiments which take advantage of the large length of the trench to allow random positioning of Au coated polystyrene microspheres to result in possible trapping. The trench geometry is also found to be convenient for optical detection. The high contrast allows direct high magnification optical microscope observation, providing a simple platform for detecting occurrences of an adequately positioned sphere. Our simpler and more scalable approach also avoids magnetic sub-layers [29] that can potentially create mechanical artifacts when applying external magnetic fields.

A dispersion of microspheres in ethanol is locally deposited over the nanotrenches using a micropipette attached to a micromanipulator. The process is performed under optical microscope observation, where occurrence of microsphere bridging can be immediately assessed. Several gaps are bridged by either a single (figure 4(a)) or a group of microspheres, and resistance measurements are performed before and after sphere deposition. Once the spheres are trapped over the gap, the resistance decreases from the open circuit value to several hundred ohms, showing an Ohmic *IV* curve (cf figure 4(b)). Using a pseudo four-point geometry, with patterned y-shaped electrodes for separate current and voltage probes, we can reproducibly observe a sample resistance below 50 Ω at room temperature. Such low-value Ohmic contact reveals that stable electrical connections can be made over the trenches. It confirms the quality of the surfaces and their adequacy for making good electrical interconnects, which is challenging when inserting a 'wet' deposition step in the device buildup or for free standing devices.

Figure 4.

4. Conclusion

In summary, we showed that several micrometers wide electrodes separated by a sub 100 nm gap can be reproducibly produced by means of simple optical lithography techniques, with a control of the electrode distance of the order of 10 nm accuracy. The process is simple and

easily scalable for high throughput fabrication, as it uses standard optical lithography techniques and allows parallel processing of many junctions. The nanotrenches are suitable for use in micro and nanoelectronics where averaging measurements over several particles contacted in parallel is important, and are well adapted to nano and microparticle interconnect based strategies. The device functionality was demonstrated by measuring the I–V transport properties of mono and multilayers of highly resistive nanoparticles from room temperature down to 50 K. A non-Arrhenius law was observed for the resistance vs temperature and interpreted in the framework of a resistor network in the presence of electron–electron interactions and structural disorder. Another example of interest of such a device was demonstrated by their use as a trap for conductive microspheres. The good Ohmic contact between the spheres and the electrodes on each side of the nanotrench and the increased probability of trapping spheres between electrodes confirmed the reliability and interest of such a kind of electrode. Both these systems demonstrate that resistance values ranging from 10^2 Ω up to 10^{12} Ω can be reliably measured, with corresponding currents from hundreds of μA down to a few tenth of pA. Owing to their peculiar geometry, the nanotrench electrodes are ideally suited when a high dynamic range of investigated current values is desired. This is especially useful for temperature-dependent studies on samples having resistance values driven by thermally activated processes. Materials with large intrinsic sheet resistance value also strongly benefit from large aspect ratios of the interconnects. It is interesting to note that the nature of the deposited material is not important for this process, as only the geometrical height of the electrodes is involved in the shadowing effect. Manufacturing gaps with two different electrode materials is therefore straightforward, in contrast with e-beam patterning strategies. This can be of particular interest when designing diodes or photo-active particles combined with molecular electronics systems. The process can also be straightforwardly extended to fabricate magnetic electrodes, of interest for spintronics applications, or to fabricate superconducting electrodes, relevant for mesoscopic physics and quantum effects.

Acknowledgments

References

[1] *For a book, see for example Tour J M 2003 Molecular Electronics: Commercial Insights, Chemistry, Devices, Architecture and Programming (River Edge, NJ: World Scientific)*

[2] *For a review, see for example Kwok K S and Ellenbogen J C 2002 Mater. Today 5 28*

[3] *Ralph D C, Black C T and Tinkham M 1997 Phys. Rev. Lett. 78 4087-90*

[4] *Klein D L, Roth R, Lim A K L, Alivisatos A P and McEuen P L 1997 Nature 389 699-701*

[5] *Reed M A, Zhou C, Muller C J, Burgin T P and Tour J M 1997 Science 278 252-4*

[6] *Tans S J, Devoret M H, Dai H J, Thess A, Smalley R E, Geerligs L J and Dekker C 1997 Nature 386 474-7*

[7] *Wu S M, Gonzalez M T, Huber R, Grunder S, Mayor M, Schonenberger C and Calame M 2008 Nat. Nanotechnol. 3 569-74*

[8] *Selzer Y, Cai L T, Cabassi M A, Yao Y X, Tour J M, Mayer T S and Allara D L 2005 Nano Lett. 5 61-5*

[9] *Salomon A, Cahen D, Lindsay S, Tomfohr J, Engelkes V B and Frisbie C D 2003 Adv. Mater. 15 1881-90*

[10] *Bachtold A, Fuhrer M S, Plyasunov S, Forero M, Anderson E H, Zettl A and Mc Euen P L 2000 Phys. Rev. Lett. 84 6082*

[11] *Dai H J, Wong E W and Lieber C M 1996 Science 272 523*

[12] *Liao J, Bernard L, Langer M, Schönenberger C and Calame M 2006 Adv. Mater. 18 2803*

[13] *Kinge S, Crego-Calama M and Reinhoudt D N 2008 ChemPhysChem 9 20-42*

[14] *Kyle J M B, Christopher E W, Siowling S and Bartosz A G 2009 Small 5 1600-30*

[15] *Pauly M, Pichon B P, Demortière A, Delahaye J, Leuvrey C, Pourroy G and Bégin-Colin S 2009 Superlattices Microstruct. 46 195-204*

[16] *Akkerman H B, Blom P W M, de Leeuw D M and de Boer B 2006 Nature 441 69-72*

[17] *Luber S M, Zhang F, Lingitz S, Hansen A G, Scheliga F, Thorn-Csanyi E, Bichler M and Tornow M 2007 Small 3 285-9*

[18] *Black C T, Murray C B, Sandstrom R L and Sun S 2000 Science 290 1131-4*

[19] *van der Molen S, Liao J, Kudernac T, Agustsson J, Bernard L, Calame M, van Wees B, Ferringa B and Schönenberger C 2009 Nano Lett. 9 76-80*

[20] *Greshnykh D, Fromsdorf A, Weller H and Klinke C 2009 Nano Lett. 9 473-8*

[21] *Zhou C, Deshpande M R, Reed M A, Jones L and Tour J M 1997 Appl. Phys. Lett. 71 611-3*

[22] *Li D Q, Bishop A, Gim Y, Shi X B, Fitzsimmons M R and Jia Q X 1998 Appl. Phys. Lett.* **73** *2645-7*

[23] *Zeng H, Black C T, Sandstrom R L, Rice P M, Murray C B and Sun S H 2006 Phys. Rev. B* **73** *020402*

[24] *de Boer B, Frank M M, Chabal Y J, Jiang W R, Garfunkel E and Bao Z 2004 Langmuir* **20** *1539-42*

[25] *Haynie B C, Walker A V, Tighe T B, Allara D L and Winograd N 2003 Appl. Surf. Sci.* **203** *433-6*

[26] *Tang J, Wang Y, Nuckolls C and Wind S J 2006 J. Vac. Sci. Technol. B* **24** *3227-9*

[27] *Fursina A, Lee S, Sofin R G S, Shvets I V and Natelson D 2008 Appl. Phys. Lett.* **92** *113102*

[28] *Poddar P, Fried T and Markovich G 2002 Phys. Rev. B* **65** *172405*

[29] *Long D P, Patterson C H, Moore M H, Seferos D S, Bazan G C and Kushmerick J G 2005 Appl. Phys. Lett.* **86** *153105*

[30] *Negishi R, Hasegawa T, Terabe K, Aono M, Ebihara T, Tanaka H and Ogawa T 2006 Appl. Phys. Lett.* **88** *223111*

[31] *Sun L F, Chin S N, Marx E, Curtis K S, Greenham N C and Ford C J B 2005 Nanotechnology* **16** *631*

[32] *Javey A, Qi P, Wang Q and Dai H 2004 Proc. Natl Acad. Sci.* **101** *13408-10*

[33] *Zabet-Khosousi A and Dhirani A-A 2008 Chem. Rev.* **108** *4072-124*

[34] *Bai J G, Chang C-L, Chung J-H and Lee K-H 2007 Nanotechnology* **18** *405307*

[35] *Bai J G, Yeo W-H and Chung J-H 2009 Lab Chip* **9** *449-55*

[36] *Müller K K-H, Herrmann J, Raguse B, Baxter G and Reda T 2002 Phys. Rev. B* **66** *075417*

[37] *Zeng H, Black C T, Sandstrom R L, Rice P M, Murray C B and Sun S 2006 Phys. Rev. B* **73** *20402*