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Fabrication of multiple nano-electrodes for molecular addressing using high-resolution electron beam lithography and their replication using soft imprint lithography

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Abstract

We investigate the ability for High Resolution Electron Beam Lithography (HREBL) to fabricate multiple nano-electrodes with the smallest gap in the smallest area. By using both standard PolyMethylMethAcrylate (PMMA) as resist and standard MIBK/IPA development, we show that up to 10 nano-electrodes can be realized in an area as small as 65 nm. The obtained structures have been used either for the realization of embedded electrodes in SiO_2 by wet etching followed by lift-off, or for the fabrication of molds for Nano-Imprint Lithography using PMMA as a mask for Reactive Ion Etching of silicon. Preliminary results on the replication of these molds using a soft nano-imprint process are also presented.

Keywords: Electron beam lithography; High resolution; PMMA; PDMS; Mold; Nano-imprint lithography

1. Introduction

Recent developments in nanotechnologies concern the connection of individual molecules like carbon nanotubes, DNA, proteins or molecular motors [1,2]. In order to probe these molecules, several electrodes are needed for current/voltage characterization or supplying. Their size must be comparable to those of the molecules probed and the distance between two electrodes must be as small as possible enabling trapping or in-between deposit of the molecules. In the case of molecular electronic or DNA connection the typical need is three electrodes commonly referred as source, drain and gate in order to investigate transistor effect with molecular material. In the context of nanomachines where, for example, the purpose is to induce rotation of an individual molecule through current injection, more than three electrodes can be required. We have earlier demonstrated [3,4] that

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HREBL allows us to produce isolated structures with a dimension down to 3–5 nm and to achieve dots arrays exhibiting an areal density of 750 Gbit/inch^2. We have thus decided to investigate in detail the ability for HREBL to fabricate those multi nano-electrodes and tackle the following questions: what is the smallest gap achievable between two electrodes, how many nano-electrodes can we settle in a molecular size area.

2. Experimental

For these experiments we use bulk silicon substrates with 100 nm of thermally grown oxide for embedded electrodes technology. HREBL experiments were carried out using a modified transmission electron microscope (TEM), operating at 200 kV, with scanning capabilities (CM20—Philips) and equipped with a field emission gun. The beam scanning is controlled by a 16-bit external pattern generation system coupled with a Computer Assisted Design software and hardware from JC Nabity Lithography Systems. After completion of the nanofabrication process, structures can be observed in Scanning Electron Microscopy (SEM) using the same machine. A specific calibration of the magnification ensures dimensional measurement accuracy better than 5%.

Patterns of multiple nano-electrodes are composed of pointed contact pads homogeneously distributed on a circle (D) of 200 nm diameter (Fig. 1). Their width (L) is 400 or 200 nm in the case of more than six nano-electrodes. Small nanometric lines terminate these pads and converge in a central region where the 'molecular size' inter-electrode gap is defined. These lines are fabricated using a single scan of the electron beam. In order to adjust the final size of the inter-electrodes region, we have chosen to modify the length of these terminal lines while keeping the exposure dose constant. This strategy can give, to our mind, better reproducibility than the one consisting in changing the exposure dose for a constant length of the lines. The exposure doses were determined from preliminary results to 2000 μC/cm^2 for the pads and 8 nC/cm for the terminal lines, giving a

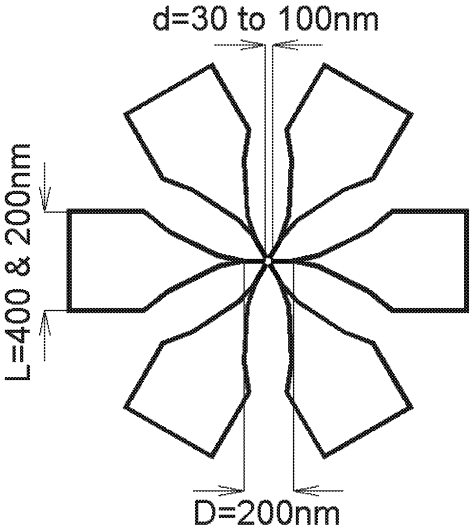

Fig. 1. Example of layout of a pattern comprising six nano-electrodes.

linewidth of 20 nm in the final part of the nano-electrodes. The geometry and size of the connecting pads is fully compatible with a metallic cantilever probes array developed in our laboratory [5] enabling future electrical characterization of these nano-junctions or molecular conductivity measurements. All samples were spin coated with a 50 nm PMMA (950.000 MW) resist layer. Developments were made in a mixture of MIBK:IPA/1:3 for 15 s and rinsed in pure IPA. The multiple nano-electrodes pattern were transferred into the silicon substrate by etching using the PMMA resist as a mask. The purpose here was to fabricate negative molds for future replication of these nano-electrodes by Nano-Imprint Lithography (NIL). For silicon etching, we use a High Density Plasma (HDP) system usually dedicated to silicon deep etching. We have optimized a new process using a SF_6:C_4F_8:O_2 mixture in order to achieve almost perfectly vertical etching without under-etching. The resulting Si and PMMA etching speeds are nearly the same: 200 nm/min.

For mold replication, we use PDMS as a thermocurable resist [6]. Molds are treated by silanization for unmolding.

For molecular addressing applications, any topographical relief on the surface can affect either the deposition of the molecules, the way these molecules anchor to the electrodes or also the imaging capability of the inter-electrode gap with an AFM tip. Following Rousset et al. [7], we have thus investigated the fabrication of embedded metallic electrodes in SiO_2. After resist development the oxide layer is wet etched in a solution of Buffered HF:H_2O/5:100 at 20 °C. After SiO_2 etching a 50 Å Ti film is deposited on the substrate followed by a 50 Å Au:Pd/80:20 film and we make a classical lift-off by dissolving the PMMA in trichloroethylene at 50 °C. The difficulty of the process is to control exactly the etching depth and the deposited metallic film thickness in order that both compensate for embedding nicely the electrodes. This requires systematic calibrations just before the process. Our process of embedded metallic electrodes was applied to patterns containing only two nano-electrodes.

3. Results

Fig. 2 shows an example of embedded electrodes that exhibit a nanogap of 7 nm and a small surface roughness. The gap between the electrodes appear very dark, this is the indication that the SiO_2 layer has been removed in the inter-electrode region due to unavoidable under-etching during the wet process. This only occurs for very small gaps. If the inter-electrode distance is enlarged to 20 nm the SEM contrast of the inter-electrode region is the same as the plain SiO_2 covered region around the electrodes.

Fig. 3 exhibits the evolution of the inter-electrode gap size as a function of the spacing coded in the layout. The vertical arrows indicate the limit where the SiO_2 top layer is completely under-etched in the gap region and the limit where the two nano-electrodes are found connected.

The evolution is very smooth indicating that the process can offer good latitude and repeatability. We have not investigated lower exposure doses than 8 nC/cm. We know that terminal lines of 10 nm can be fabricated for exposure doses around 4 nC/cm. This reduction should give nano-electrode spacing even smaller than 7 nm. However, characterization at this scale length becomes uneasy and the reproducibility of the result probably decreases. The process we have presented here with 20 nm wide nano-electrodes can be regarded as robust with respect to the ultimate resolution of our machine.

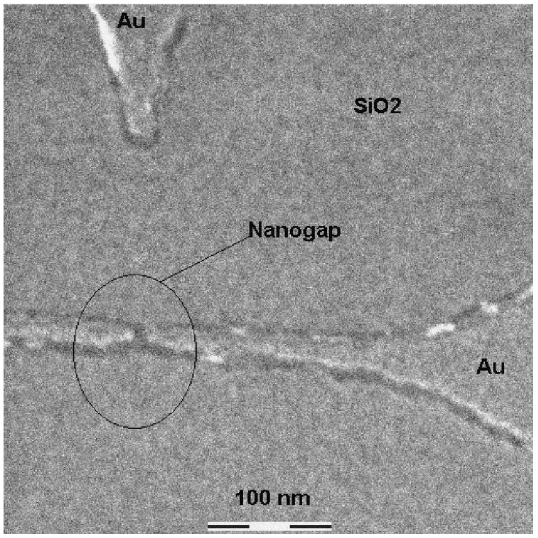

Fig. 2. SEM image of two embedded gold nano-electrodes separated by 7 nm used for carbon nanotubes connection. Lateral gate electrodes have been added for electronic transport modulation.

This is confirmed because on a same sample, all identical patterns exhibited the same 7 nm wide gap, confirming that this size can be reach with a success rate close to 100%.

Fig. 4 shows a SEM image of three, six, eight and ten nano-electrodes after ion etching. Inter-electrode area diameters of 30, 50, 75 and 65 nm are obtained, respectively, for inter-electrode coded diameters of $d = 30$, 50, 80 and 100 nm. As PMMA has not been completely etched and removed during the etching, some polymer walls around the edges can be seen in Fig. 5. After cleaning using an O_2 plasma, these polymer traces can be removed (see Fig. 6). Fig. 6 shows a SEM tilted image of a six nano-electrodes mold pattern after HREBL and 300 nm depth etching. In this example, the PMMA thickness has been increased to 300 nm in order to achieve such an etching depth. One can see that the walls are smooth and vertical.

Fig. 7 presents one of our first attempts for replicating the previously described patterns by

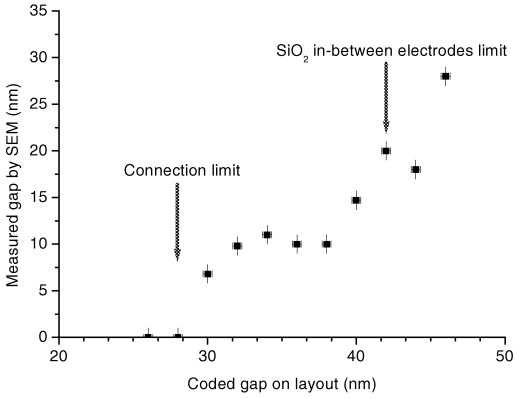

Fig. 3. Experimental evolution of the inter-electrode gap size as a function of the spacing coded in the layout of the pattern.

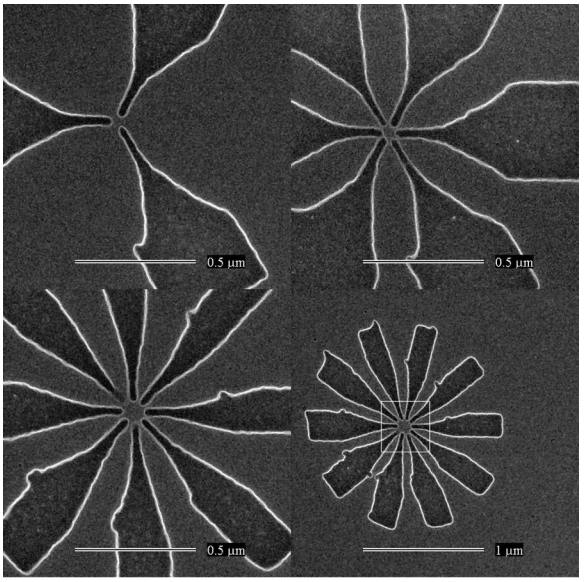

Fig. 4. SEM image of three, six, eight and ten nano-electrodes patterns after etching of the silicon substrate.

nano-imprint lithography. For this process we use PDMS as a thermocurable resist [6]. Our present results indicate the feasibility of the replication. However the first experiment using the pattern shown in Fig. 6 turned out to be difficult. We observed that the PDMS molded material is teared-off upon mold removal because of its brittle character and the very high aspect ratio of 15 (nano-electrodes of 20 nm etched down to 300 nm) of the mould. This problem leads to unresolved inter-electrode gaps.

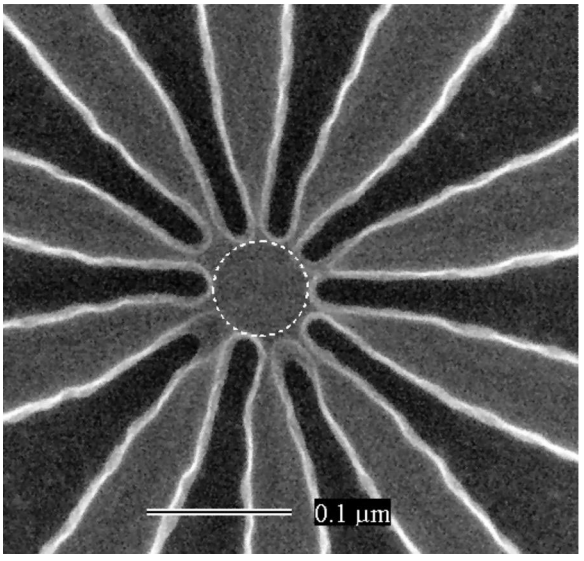

Fig. 5. Enlarged SEM image of the ten nano-electrodes pattern exhibiting an inter-electrode area diameter of 65 nm (dotted circle).

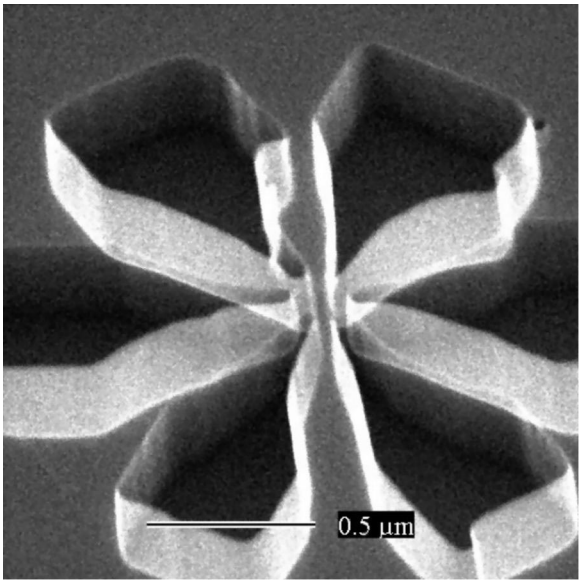

Fig. 6. SEM tilted image of a six nano-electrodes mold pattern after HREBL and 300 nm depth etching of silicon and O_2 plasma cleaning.

The presence of the very small structures on the samples after NIL confirms that our replication process does have sufficient resolution but material engineering must be optimized for enabling soft mold removal.

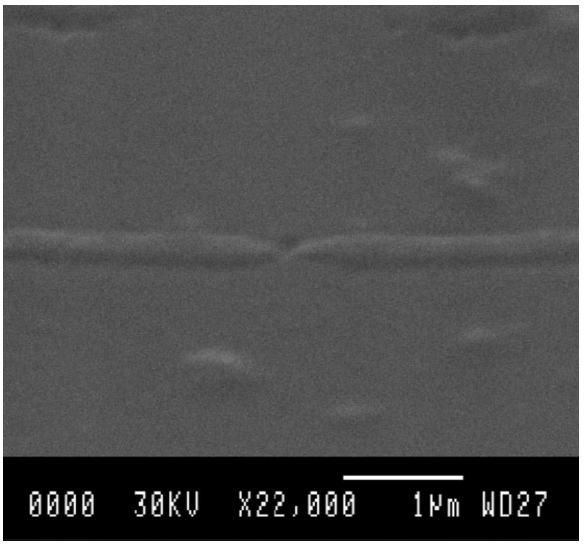

Fig. 7. SEM image of a pattern of two nano-electrodes (200 nm wide, separated by a gap of 50 nm) imprinted in PDMS using a negative master.

4. Conclusion

In this work, we demonstrate that using HREBL one can achieve multiple electrodes arranged around a central region exhibiting diameters ranging from 30 nm for three nano-electrodes to 65 nm for ten nano-electrodes. Standard exposure and development conditions of PMMA resist lead to a yield close to 100%. Experiments are in progress in order to decrease the size of the electrodes by using a pure isopropylic alcohol developer with ultrasonic agitation [4] and by optimizing the exposure doses. Molds for Nano-Imprint Lithography can be successfully fabricated and first replications using a thermocurable resist have been shown.

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