Physics and Nanosciences - PhD XXXVII cycle - Annual report - 09/2023 - German Lanzavecchia

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Research activity

The research activity is carried on within the project DNA-FAIRYLIGHTS, which will extend the concept of DNA data storage by arranging plasmonic and light-emitting particles along the DNA strand and thus will allow multiplexed data encoding with direct optical and electrical readout through nanopores.

In this context, last year we developed a method to fabricate metallic nanopores via plasmonic photochemistry on top of dielectric nanopillars. To characterize the nanopores fabricated using this approach, we conducted electrical translocation of nanoparticles and DNA molecules. The results obtained allowed to confirm the versatility of this method to produce a wide range of nanopore diameters from over 100 nm down to sub 5 nm, with the ability to detect a wide variety of entities. We additionally performed enhanced optical measurements that confirm the ability of these metallic nano rings to confine and enhance the electromagnetic field on the structures.

This work has been published in the article listed below [1]. However, the signal to noise ratio obtained in the DNA translocations was low, not being able to distinguish folded and unfolded events, and the voltage required for particle translocations was very high with a low event rate, possibly due to the high aspect ratio of the structures (cylindrical geometry). Therefore, we consider the fabrication of conical nanopores, reminiscent of widely used glass nanopipettes.

To fabricate different three-dimensional conical structures with nanopores, we spin coat on a SiN membrane with S1813 photoresist. On the bottom side, a layer of 3 nm Ti/20 nm Au is sputtered to make the sample conductive. In order to fabricate conical hollow structures, a layered pattern with decreasing size is drilled with FIB onto the sample from the bottom side, leaving a nanometer-sized aperture on the top side. While drilling the hollow structure, secondary electrons harden a layer of photoresist of about 50 nm. The unhardened resist is then removed with acetone, obtaining the desired conical nanotips.

We performed current rectification measurements on these structures that resulted in the deformation of the structure after some cycles. For that reason, we developed a method to fabricate the same kind of structure made in more robust silicon oxide, once again resembling glass nanopipettes. Before removing the unhardened photoresist, we deposit a layer of dielectric of 20 – 35 nm SiO_2 via atomic layer deposition, which also gives the possibility to use also Al_2O_3 and TiO_2. The unhardened resist can be removed with acetone, but the hardened photoresist a layer is extremely hard to remove: standard oxygen plasma cleaning methods leaves a crust of about 30 nm. Reactive Ion Etching oxygen cleaning was also performed with no significant removal of this crust even after 15 minutes of processing.

In order to facilitate the removal of the resist, we exposed the sample under UV light order to break the cross linking in the polymer, followed by low power oxygen plasma ICP-RIE for up to two minutes and a half, which resulted in an effective removal of the photoresist layer. Longer processing resulted in damaging the sample. The resulting structure can be seen in Fig. 1, a-c) before removing the resist and d-g) where the walls of the nanotips are 20 to 30 nm SiO2 and h) 30 nm TiO_2, and the nanopores shown have diameters of 15 to 40 nm. We performed EDS analysis to confirm the deposition of the dielectric and the removal of the photoresist.

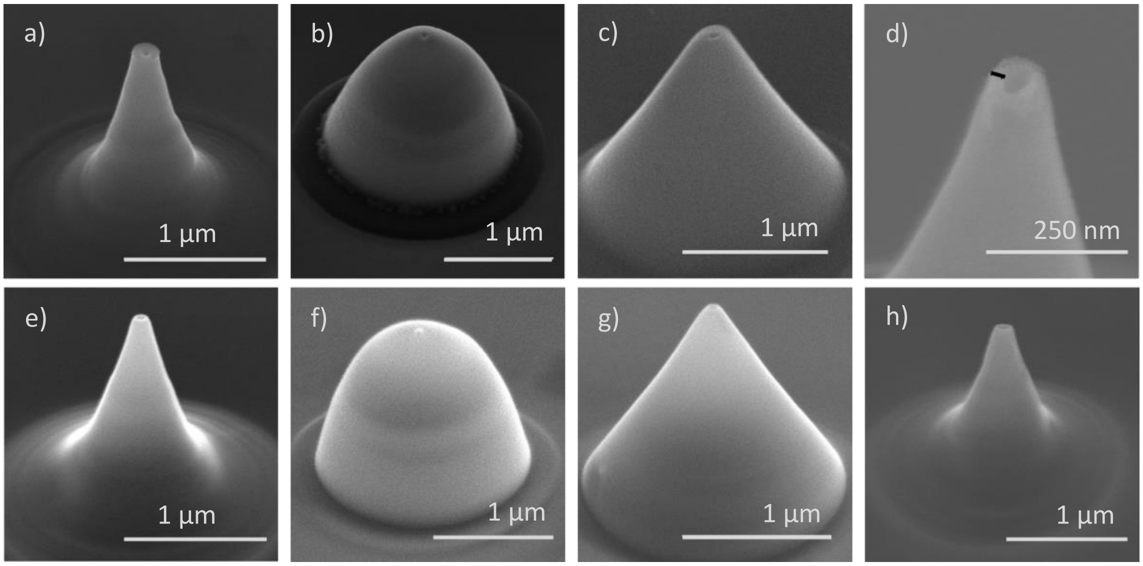

Fig. 1. SEM Micrographs of nanotips: a) convex, b) concave and c) straight profiles before removing the hardened photoresist. e) Convex, f) concave and g) straight profile in SiO_2. d) Detail of the tip of a convex nanostructure in SiO_2, the black bar is 20 nm. h) Convex profile in TiO_2.

Using this approach, we can fabricate arrays, arbitrary arrangements and single nanopores on top of designed conical structures made of different dielectric oxides. This tunability of the profile and the various materials available, can be used for modifying the ionic transport and current rectification, as well as to optimize the nanopores for the translocation of different analytes.

Besides the main focus in nanopore fabrication, I also took part in the following activities: optimization of the optical setup for single molecule analyses, such as FCS, FCS in Zero Mode Waveguides, single quantum dots immobilized on silicon substrates, and eventually translocation through nanopores; the fabrication of nanopores on SiN membranes to study the ionic current rectification and the effect of different materials and surface chemistries; design and fabrication of microfluidic cells and Silicon Nitride membranes with different sizes and chips optimized for various applications.

Courses

Introduction to nanofabrication, Course and Exam passed
Observational Astronomy, Exam passed

Publications

1. Lanzavecchia, G., Kuttruff, J., Doricchi, A., Douaki, A., Kumaranchira Ramankutty, K., García, I., Lin, L., Viejo Rodríguez, A., Wågberg, T., Krahne, R., Maccaferri, N., & Garoli, D. (2023). Plasmonic Photochemistry as a Tool to Prepare Metallic Nanopores with Controlled Diameter for Optimized Detection of Single Entities. Advanced Optical Materials. doi.org/10.1002/adom.202300786

Conferences

Oral presentation: CLEO Conference, San José, California, USA, 7-12/05/2023
Poster: Single-molecule Protein Sequencing (SMPS), Delft, Netherlands, 31/10/2022 – 03/11/2022