## High aspect ratio nanostructured surfaces by metal assisted chemical etching of silicon in gas phase

L. Romano<sup>a,b</sup>,

Z. Shi<sup>a,b</sup>, K. Jefimovs<sup>a</sup>, M. Stampanoni<sup>a,b</sup> <sup>a</sup> Paul Scherrer Institut, 5232 Villigen PSI, Switzerland; <sup>b</sup> Institute for Biomedical Engineering, University and ETH Zürich, 8092 Zürich, Switzerland; lucia.romano@psi.ch

What is the difference between microfabrication and nanotechnology? Scientists struggle all around the world to scale down the device feature size by top-down techniques such as plasma etching with specialized cryogenic gases and electrode design. However, a bottom-up approach is the natural and cost effective choice of nanofabrication. In this regard, metal assisted chemical etching (MacEtch) bypasses the limits of aspect ratio with a local electrochemical reaction that occurs only at the nanoscale of the catalyst surface. We propose the concept of inducing the MacEtch reaction in the gas phase in order to promote MacEtch among the dry etching techniques. High aspect ratio nanostructuring requires high precision pattern transfer with highly directional etching. In this work, we demonstrate the fabrication of structures with unprecedented ultra-high aspect ratios up to 10'000:1 in the nanoscale regime (feature size down to 10 nm) by MacEtch of silicon in gas phase<sup>1</sup>. Such capability opens a new world of possibilities for nanofabrication in several fields.

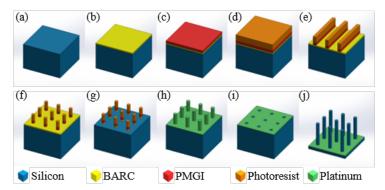
As a proof-of-concept, we successfully etched X-ray optical structures, where the control of feature size, roughness and precision of pattern transfer are fundamental for the performances of the application. By combining displacement Talbot lithography<sup>2</sup> with gas-MacEtch (see Fig.1) we realized periodic arrays of sharp vertical nanopillars (see Fig.2) 250 nm-thick and up to 50 µm-long on large area (~cm<sup>2</sup>).

The method is an interesting and promising low-cost technology for producing high aspect ratio nanostructures bypassing the nanoscale limits of reactive ion etching. It has high potential as nano- and micro-fabrication technique for applications, where silicon high aspect ratio nanostructures are required, for example X-ray optics, photonics, MEMS, sensors and nanostructured bio-interfaces used to both stimulate and sense biological systems<sup>3</sup>.

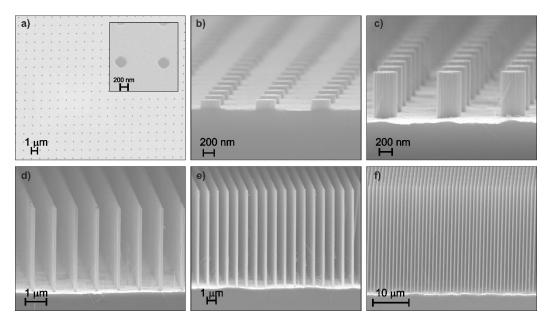
L. Romano, M. Kagias, J. Vila-Comamala, K. Jefimovs, L.-T. Tseng, V. A. Guzenko, and M. Stampanoni, Nanoscale Horizons **5**, 869 (2020).

<sup>&</sup>lt;sup>2</sup> Z. Shi, K. Jefimovs, L. Romano, and M. Stampanoni, Japanese Journal of Applied Physics **60**, SCCA01 (2021).

<sup>&</sup>lt;sup>3</sup> S. G. Higgins, M. Becce, A. Belessiotis-Richards, H. Seong, J. E. Sero, and M. M. Stevens, Advanced Materials **32**, 1903862 (2020).



*Figure 1: Process flow of Si nano-pillars array fabrication.* (a) Bare <100> silicon wafer, (b) spin-on bottom anti-reflective coating (BARC), (c) spin-on Polymethylglutarimide (PMGI) lift-off resist, (d) spin-on photoresist, (e) first displacement Talbot lithography (DTL) exposure, (f) second DTL exposure, (g) BARC etching, (h) platinum e-beam evaporation coating, (i) lift-off and thermal treatment, (j) gas-MacEtch.



*Figure 2: Nanopillars:* (a) plan view SEM of the Pt pattern after lift-off and thermal treatment, high magnification in the insert. (b-f) SEM in cross section of nanopillars realized by gas-MacEtch with different etching rates. With a low HF content in the liquid, the etching time of: 10 min (b), 20 min (c) and 1 h (d). With a high HF content in the liquid, the etching time of: (e) 1 h and (f) 2 h.