

Metal assisted chemical etching: towards CMOS compatible catalyst for high aspect ratio nanostructures

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For semiconductor fabrication processes, lithography, thin film deposition, and etching all play significant roles. However, with respect to plasma etching, typical limits include achievable aspect ratio at nanoscale, vertical sidewall, and ion beam damage.

Metal assisted chemical etching (MacEtch) is a plasma free, anisotropic chemical etching method that uniquely defies the isotropic nature of conventional wet etching, through local catalyzed electrochemistry. The patterned metal catalyst films can also locally enhance the etching rate of various semiconductors, enabling MacEtch to realize spatially defined 3D nano-structures with potentially huge aspect ratios (up to 10'000:1)¹. Our recent demonstrations of MacEtch in gas-phase, including those from the community, explicitly open the path to processing scalability and set the foundation for translating this technique from lab to fab. This work reviews the fundamentals of the method, the open challenges, and the recent milestones, pointing out the new possibilities in several different fields, such as X-ray optics microfabrication, plasma damage free 3D electronics, photonics, sensors, quantum and biomedical devices. Utilizing gas-MacEtch, we realized periodic arrays of sharp vertical Si nanopillars hundreds of nm-thick and up to 50 μm -long on a large area (in cm^2 range) using platinum as a metal catalyst, HF vapor as the etchant, and oxygen as the oxidant². We present here, the etching rate of silicon as a function of resistivity range, doping type and utilizing different catalysts. Ruthenium is a CMOS compatible catalyst however, the typical use of H_2O_2 as an oxidant results in very porous silicon structures³. We mark a new milestone for a CMOS compatible MacEtch process for high aspect ratio Si nanostructures with very low porosity using Ru as a very reactive catalyst for oxygen based gas-phase etching.

¹ L. Romano, M. Kagias, J. Vila-Comamala, K. Jefimovs, L.-T. Tseng, V. A. Guzenko, and M. Stampanoni, *Nanoscale Horizons* **5**, 869 (2020).

² Z. Shi, K. Jefimovs, M. Stampanoni, and L. Romano, *Materials Science in Semiconductor Processing* **157**, 107311 (2023).

³ A. Mallavarapu, P. Ajay, C. Barrera, and S. V. Sreenivasan, *ACS Applied Materials & Interfaces* **13**, 1169 (2021).

MacEtch for high aspect ratio structures

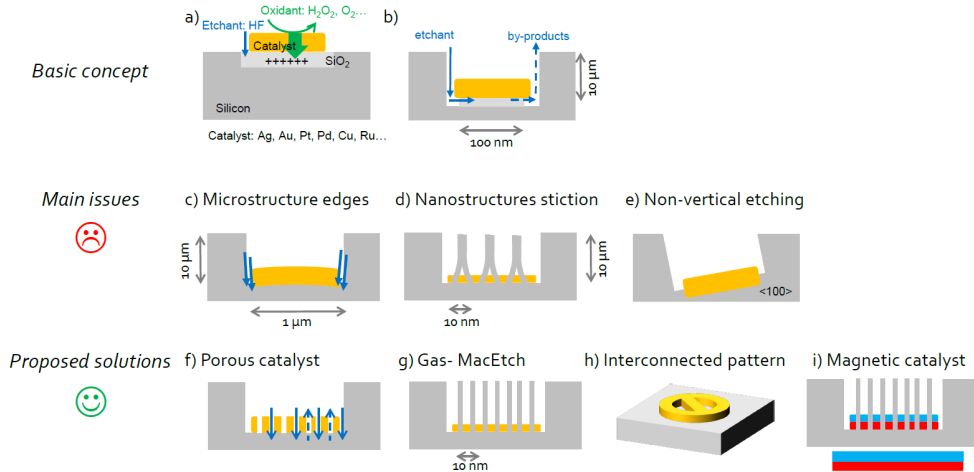


Figure 1: MacEtch: schematic of MacEtch mechanism, main issues for high aspect ratio structures and proposed solutions.

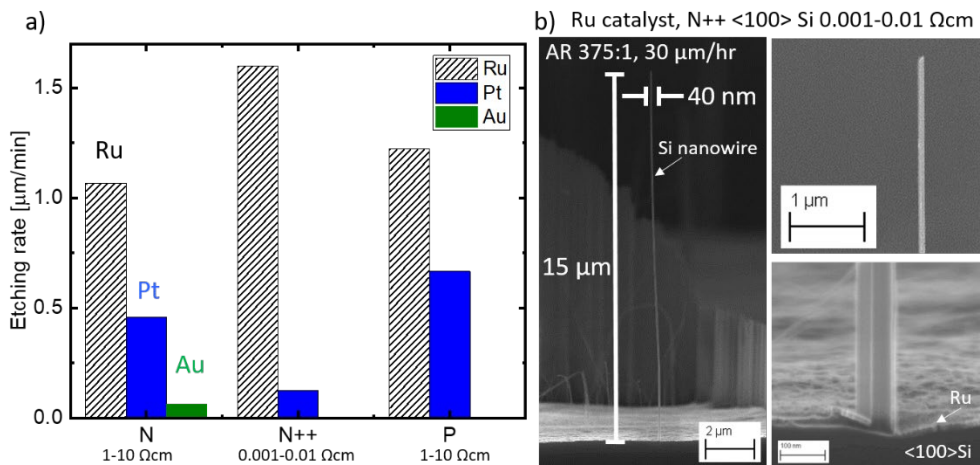


Figure 2: Etching rate and nanostructures of gas-MacEtch: a) etching rate measured for different catalysts (Ru, Pt, Au) and <100> silicon substrates with different doping in the same etching conditions², Ru has the highest chemical reactivity with oxygen that is reflected in the highest etching rate being the etching process limited by the oxygen flow; b) high aspect ratio nanowire (SEM in side view with high magnification of bottom and top of the nanowire) etched in silicon by gas-MacEtch with oxygen as reactant and Ru as catalyst with etching rate of 30 μm/hr at 60°C.