Catalyst motion in Metal-assisted Chemical Etching

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Complex 3D geometry can be etched in silicon using Metal-assisted Chemical Etching (MacEtch) by properly controlling catalyst shape. Understanding the mechanism driving catalyst motion is required when trying to etch specific or complicated geometry. This seminar provides experimental evidences shown that Derjaguin and Landau, Verwey and Overbeek (DLVO) encompassed forces drive catalyst motion in MacEtch.

As shown in Figure 1, in MacEtch a metal catalyst is used to generate a local galvanic cell across the catalyst that locally increase the dissolution rate of silicon in an etchant solution of hydrofluoric (HF) acid and hydrogen peroxide (H_2O_2). Unlike other etching techniques were a pattern of material remains on the top surface acting as a mask, in MaCE the metal catalyst moves into the substrate at the silicon around and beneath the catalyst dissolves. Because the catalyst can travel in 3 dimensions while continuing to etch it is possible to create 3D patterns in the silicon with straight, curved, helical, and random, etching paths reported for Pt, Au and Ag nanoparticles and colloids. More recently, our group has reported on the effects of catalyst shape on etching direction and showed that cycloids, spirals, sloping channels, "S" shaped channels and more can be fabricated by controlling catalyst shape to create complex, 2D and 3D nanostructures with extremely smooth walls.. [1-3]

DLVO forces drive catalyst motion. The experimental evidence presented in this study include path and deflection analysis of complex catalyst systems and distance-displacement measurements from in-situ Atomic Force Microscopy (AFM). These forces were found to exert between 11 MPa and 18 MPa of attractive pressure differentials across the catalyst and operate over extremely short distance of ~4 nm. These values were within theoretical predictions. The

(1) Hildreth, O.; Lin, W.; Lin, W.; Wong, C.-P. Effect of Catalyst Shape and Etchant Composition on Etching Direction in Metal-Assisted Chemical Etching of Silicon to Fabricate 3D Nanostructures. *ACS Nano* **2009**, *3*, 4033–4042.
(2) Hildreth, O.; Fedorov, A. G.; Wong, C.-P. 3D Spirals with Controlled Chirality Fabricated Using Metal-Assisted Chemical Etching of Silicon. *ACS Nano* **2012**, *6*, 10004–10012.
(3) Hildreth, O.; Rykaczewski, K.; Fedorov, A. G.; Wong, C. P. A DLVO Model for Catalyst Motion in Metal-Assisted Chemical Etching Based Upon Controlled Out-of-Plane Rotational Etching and Force-Displacement Measurements. *Nanoscale* **2013**, *5*, 961–970.

highly non-linear nature of these forces means that MacEtch is extremely sensitive to local etching conditions and parameter optimization is necessary to control etch path.

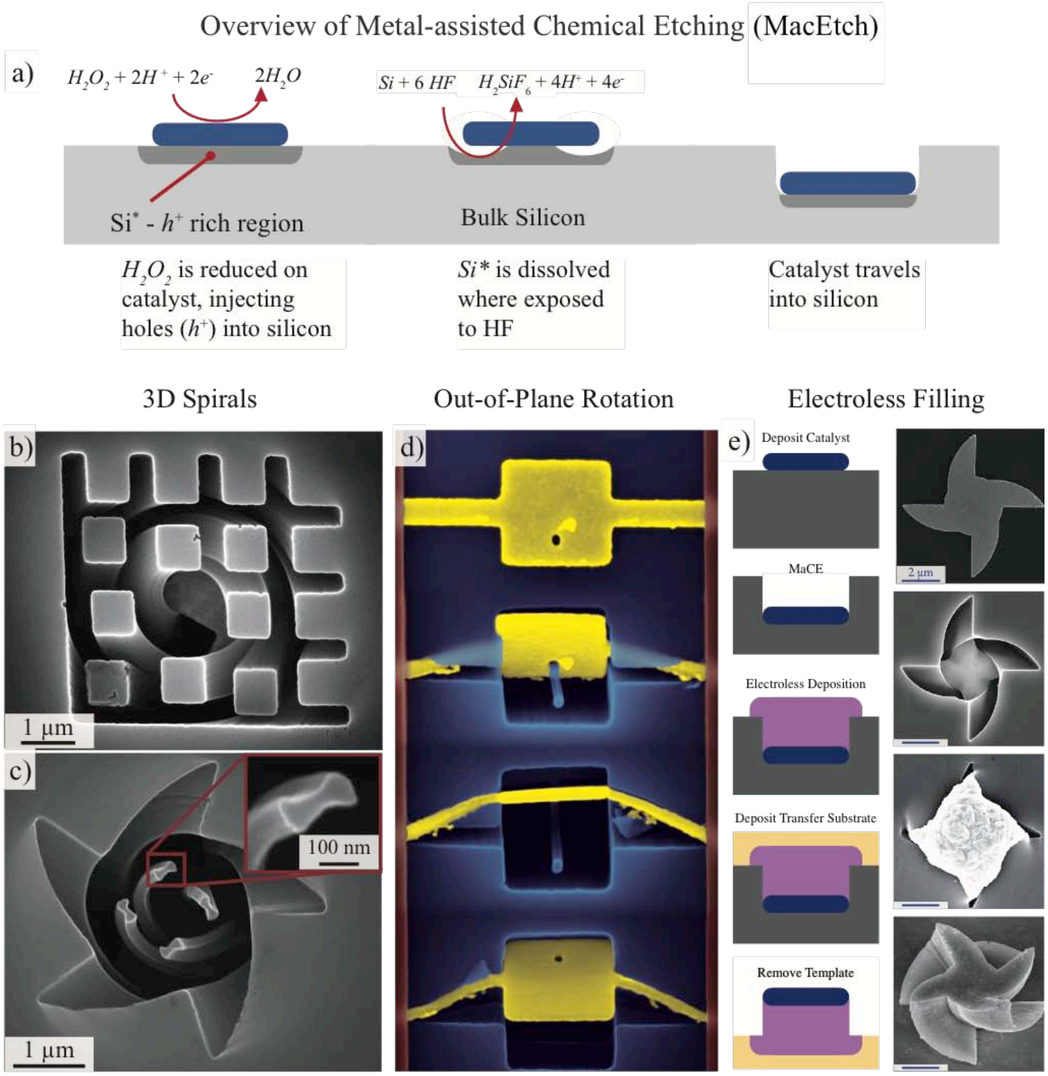

Figure 1: Overview of MaCE. (a) overview of the base chemical reaction. H_2O_2 is reduced on the catalyst and holes (h^+) are injected into the silicon – creating a hole (h^+) rich region of silicon that is readily dissolved by HF. van der Waals forces pull the catalyst into the substrate to propagate the reaction. (b-c) example spiral structures fabricated using MacEtch. (d) out-of-plane rotation. (e) example on how to use MacEtch as a template to fabricate 3D structures using electroless deposition.