Etching very large features by metal-assisted chemical etching

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Metal-assisted chemical etching (MACE) of Si has been known for more than a decade[1]. It is used for etching nano-structures such as Si nanowires that can be sub-100 nm in diameter and micrometers long[2]. The high resolution capacity, simplicity, applicability to various substrates, and cost efficiency of the technique make it one of the most popular etching techniques. During the etching, the etching solution must be able to flow underneath of the metal layer to etch the silicon there. But for large structures, it is very challenging for the solution to travel long distance laterally through underneath the metal film. As a result, the etching of large recessed structures would be very slow, if not impossible. Indeed, as shown in Figure 1 as an example, the un-patterned area in the center of nanowires is etched far slower than the rest area. Only very recently, Kim *et. al.* were able to etch uniform micro-scale features by depositing thin discontinuous island-like layers of noble metal catalysts (5 nm Ag followed by 10 nm Au) that just allow fluid to flow underneath of the noble metals to carry out the etching[3]. Here, we show an alternative and much more robust way of etching extremely large features in Si by carrying out MACE on porous substrate pre-structured by low cost maskless *electrochemical* etching of a bare silicon wafer. The etching works because gold film coated on porous silicon consists of numerous random sub-30 nm holes to allow etchant flowing to below gold film, whereas the holes are small enough to allow silicon right below the holes get etched as well.

A standard MACE process consists of oxidation and reduction reactions occurring at metal-Si interface. In a typical MACE solution, H_2O_2 is used to oxidize the Si, and HF to etch the oxidized Si layer. The noble metal is a catalyst that reduces H_2O_2 by giving electrons which results in injecting hole carriers into Si. The Si surface which is not in direct contact with metal catalyst will be etched far slower, which allows the noble metal sink into Si to process etching.

In this work, firstly, 100 oriented, n-type, 0.001-0.002 ohm·cm Si wafer is etched by electrochemical etching to generate a porous layer on the surface. The maskless electrochemical etching was performed in a standard Teflon etching cell using HF:EtOH:H_2O solution (volume ratio of 1:6:43), under 5 V bias (32 mA/cm^2 current density) for 1 minute. It should be noted that the sample was partially in contact with the etching solution that allows a comparison between porous and non-porous regions of the sample after MACE. The electrochemical etching resulted in sub-30 nm pores with hundreds of nanometer spacing. Next, 40 nm Au layer was coated on the porous Si by electron beam evaporation, and for a quick test, large random Au patterns were formed by scratching the sample surface mechanically that leads to peeling off of Au layer in some regions. Afterward, the MACE process was carried out in HF:H_2O_2:H_2O (volume ratio of 9:1:40) solution for 60 minutes at room temperature. The results are shown in Figure 2, where a very impressive large structure of hundreds of micrometer was etched 8.5 µm deep into Si. The etching uniformity and etch rate can vary depending on the depth, density, and size of the pores, as well as the thickness of the metal layer. As a future work, we are working to optimize the process and pattern features using lithography tools to show process' applicability to nano-micro fabrication.

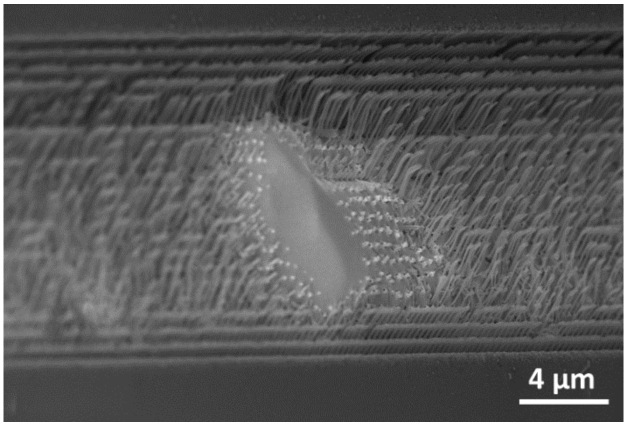

Figure 1: SEM image of non-uniformly etched nanowires after MACE, showing much slower etching of the central microscale feature than the surrounding nanoscale features.

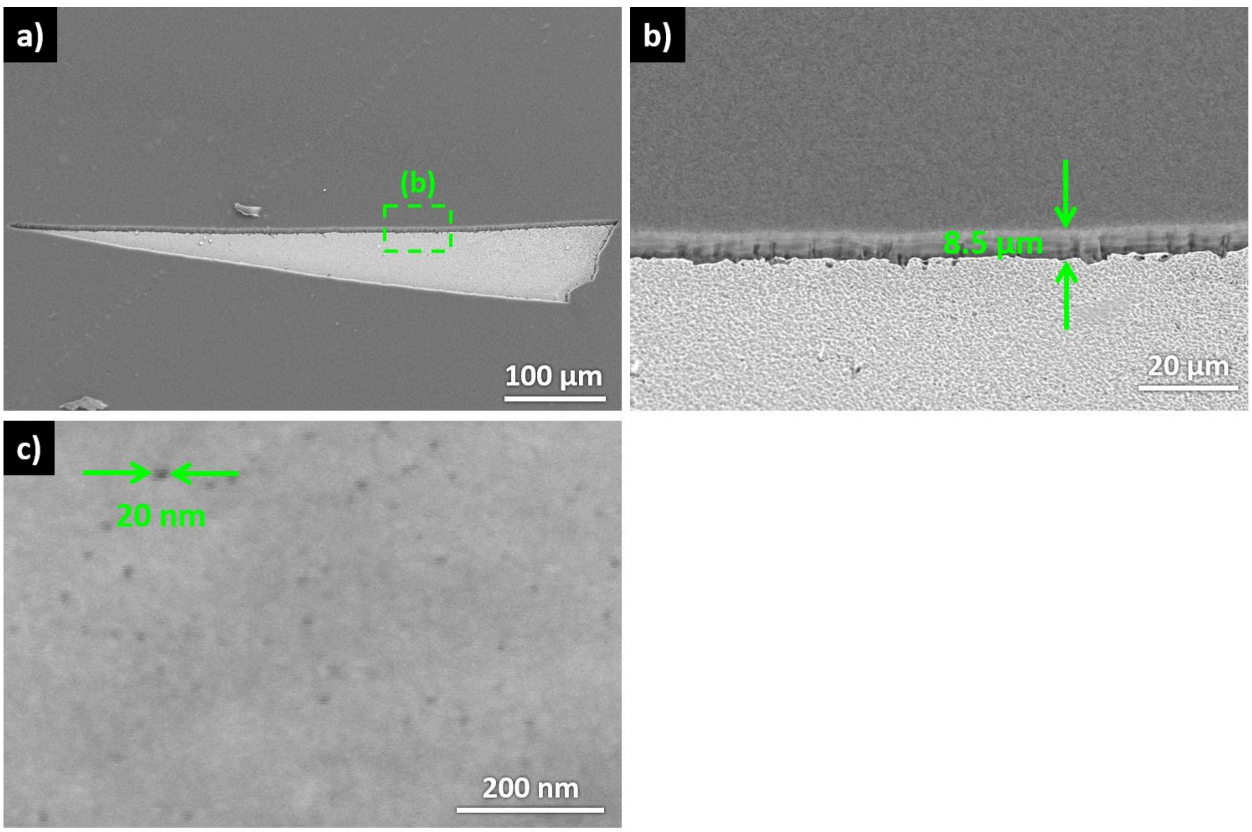

Figure 2: SEM images of a very large feature etched by MACE. Figure 2c shows porous Au surface. The gold film is porous when coated on porous silicon having random pore size and location, obtained by very low cost maskless electrochemical etching of a bare silicon wafer.

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[2] S.W. Chang, V.P. Chuang, S.T. Boles, C.A. Ross, C.V. Thompson, *Adv. Funct. Mater*, 19, 2495 (2009)
[3] S.-M. Kim, and D.-Y. Khang. *Small* 10.18, 3761 (2014)