Fabrication of local areas of high aspect ratio silicon structures using metal-assisted chemical etching - MACE

A technology platform for the creation of 3D templates

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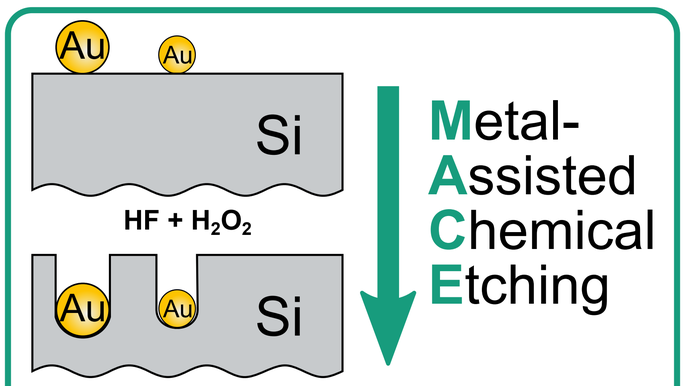
Background

The ongoing miniaturisation of integrated devices comes along with the demand of smaller feature scales in combination with an increasing aspect ratio. 3D structures can be fabricated by a bottom-up approach to omit cost intensive high precision lithography processes. Here, we present a technology to fabricate integrated 3D silicon structures with high aspect ratios using metal-assisted chemical etching (MACE).[1]

MACE is a wet etching process which uses a noble metal - like gold - to selectively etch silicon at the metal-silicon interface. Silicon is etched in a solution of aqueous hydrofluoric acid (HF) and hydrogen peroxide (H_2O_2) in the presence of gold.

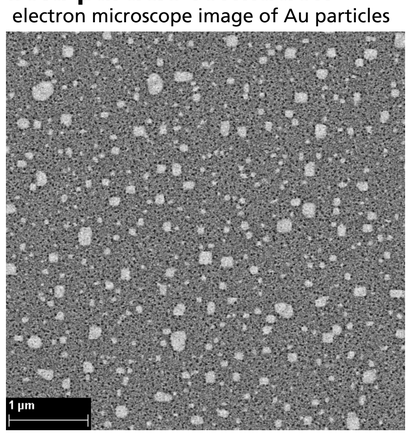
H_2O_2 is reduced at the noble metal interface within the acidic solution generating electron vacancies h^+ **(1)**. The parameter *n* depicts the number of involved electrons. Two mechanisms may occur **(2)**: ***n*=2**, the pore formation with direct silicon etching, ***n*=4**, the electropolishing: Si will be oxidised to SiO_2, which is etched by HF.[1]



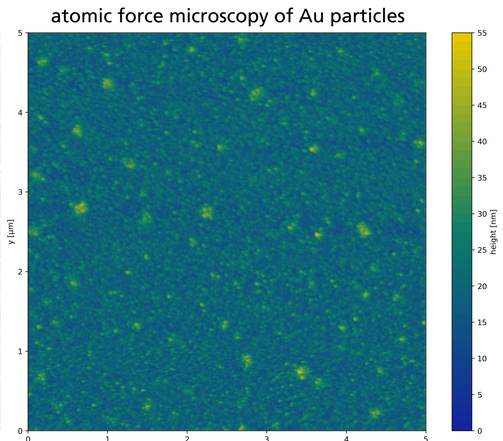
(1) $H_2O_2 + 2H^+ \rightarrow 2H_2O + 2h^+$
(2) $Si + 6HF + nh^+ \rightarrow H_2SiF_6 + nH^+ + (2\text{-}0.5n)\ H_2$ [1]

Gold particle formation

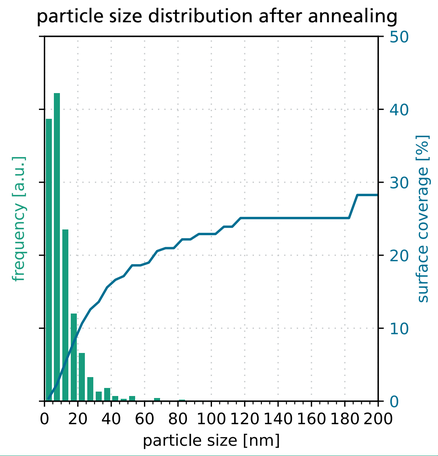
electron microscope image of Au particles



atomic force microscopy of Au particles



particle size distribution after annealing



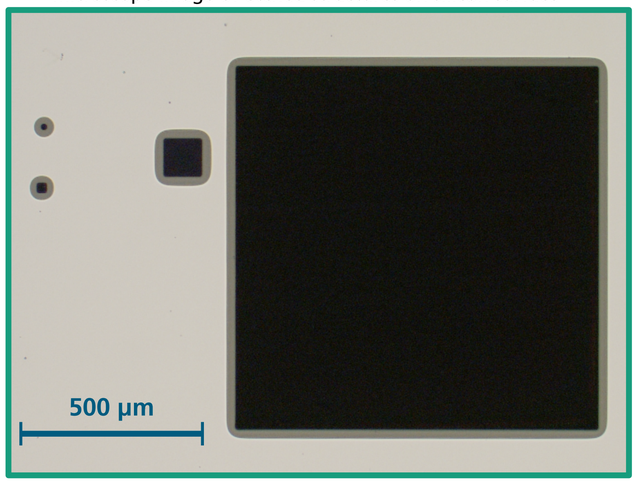
Experimental

- p-doped 150 mm Si wafers coated with 5 nm Au
- annealing at 300 °C for 30 min for particle formation
- parylene C pattern as masking layer - rectangular testing fields
- wet etching in $HF:H_2O_2:H_2O$
  - HF concentration: 1.7 mol/L
  - H_2O_2 concentration: 0, 50, 145, 190, 240 mmol/L
  - etching time: 10 min
- analysis with scanning electron microscopy, atomic force microscopy, optical microscopy, and spectral reflectometry

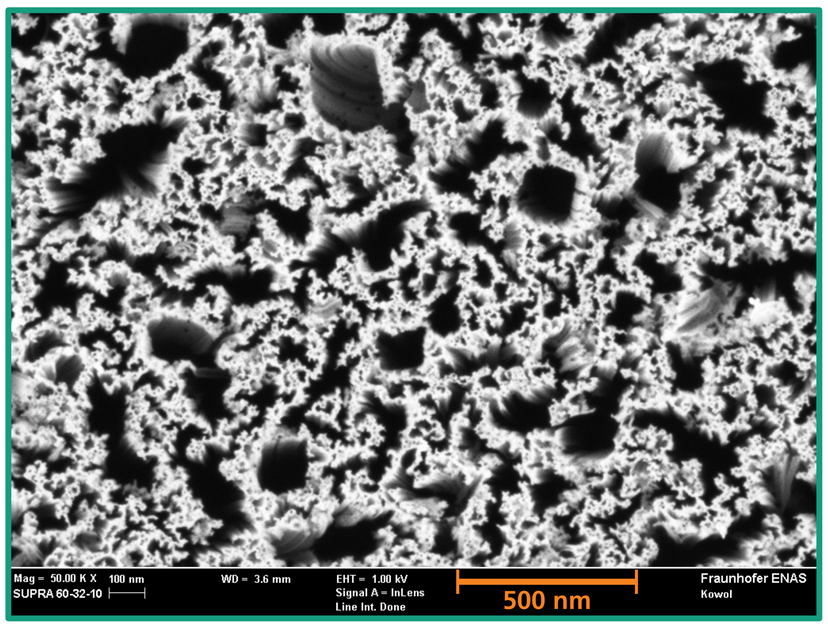
Etched silicon

- 3D structures createdd in defined areas
- Au particles remain at bottom of trenches
- surface of etched area dark: black silicon.

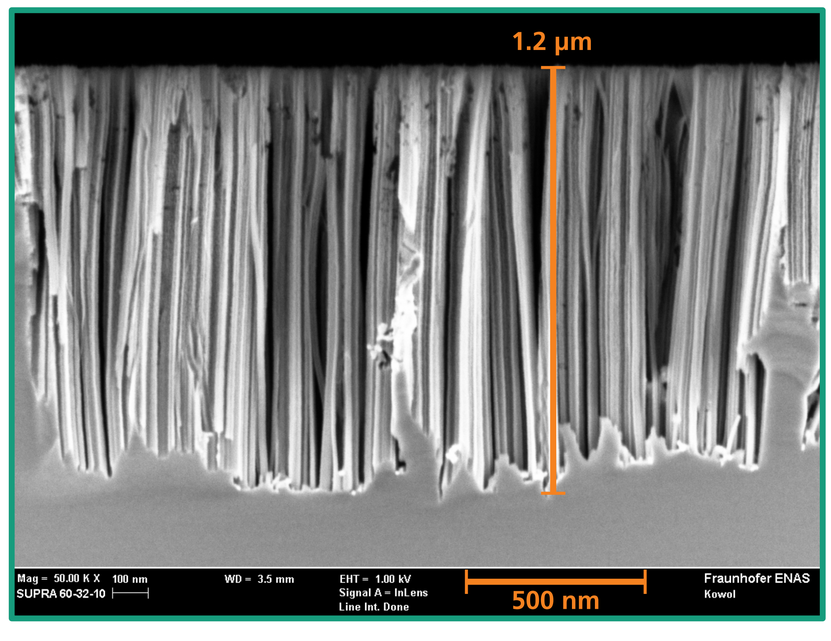
microscope image of etched structures on silicon surface



scanning electron microscope image of etched surface

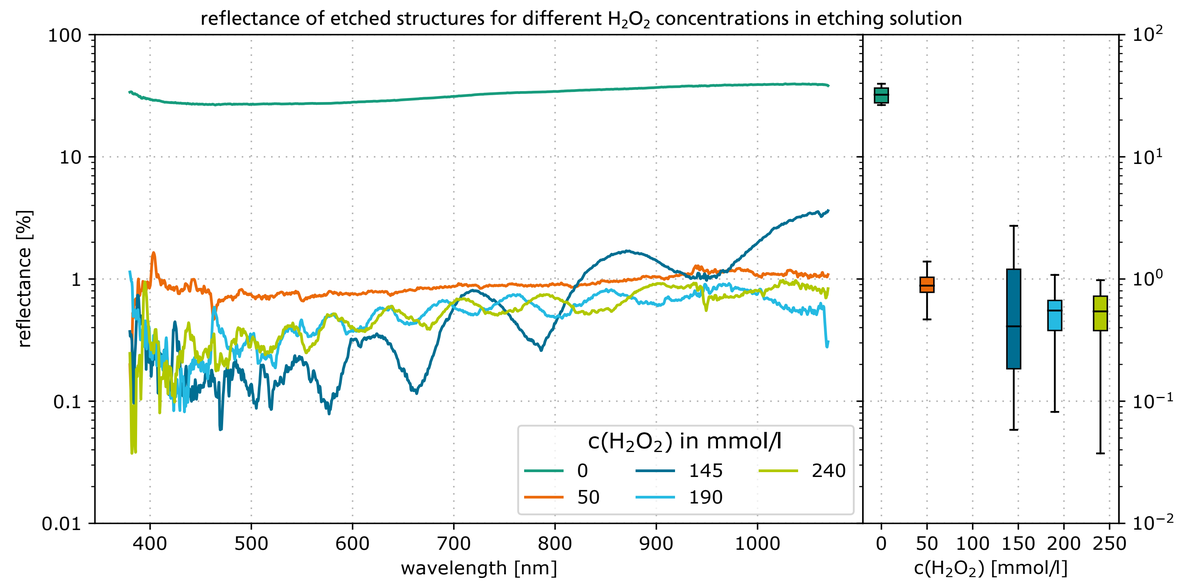


scanning electron microscope image (cross section) of 3D structures



black silicon - reflectance

reflectance of etched structures for different H_2O_2 concentrations in etching solution



Conclusion

Here, we successfully demonstrated a low-cost bottom-up approach for the fabrication of 3D silicon structures with high aspect ratios on wafer-level.

The wet etching process using self-assembled Au nano-particles resulted in local areas with black silicon structures.
The 10 min wet etching process resulted in a etching depth of 1.2 to 1.7 µm. The resulting structures are mainly vertical pillars and ribbons with typical wall sizes of ≈ 20 nm.
The special geometry creates an high absobance for visible light. This results in a reflectance of below 1% for a wide wavelength range.

This gives a technology platform for a local integration of 3D structures on chip level. These templates can be further functionalised for capacitors, gas sensors, radiation sensors and so on.

[1] M. Franz, R. Junghans, P. Schmitt, A. Szeghalmi, and S. E. Schulz, “Wafer-level integration of self-aligned high aspect ratio silicon 3D structures using the MACE method with Au, Pd, Pt, Cu, and Ir,” Beilstein J. Nanotechnol., vol. 11, pp. 1439–1449, Sep. 2020, doi: 10.3762/bjnano.11.128.

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