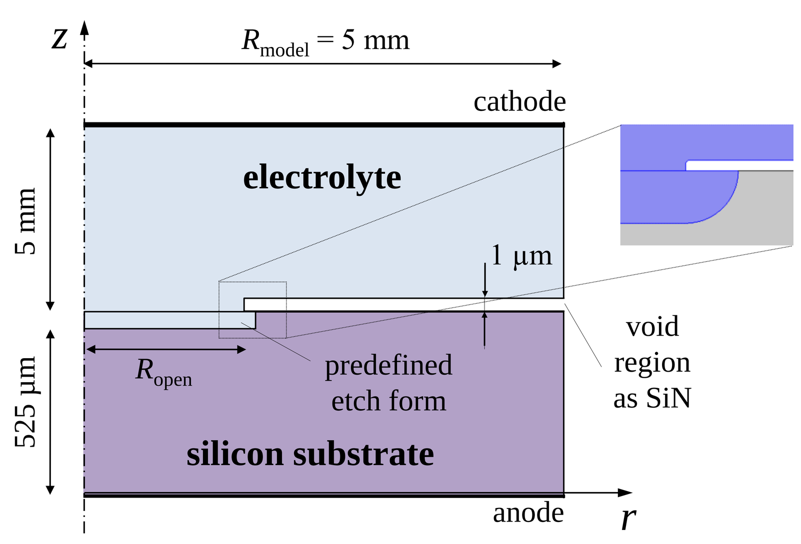
Primary Current Distribution Model for Electrochemical Etching of Silicon Through a Circular Opening

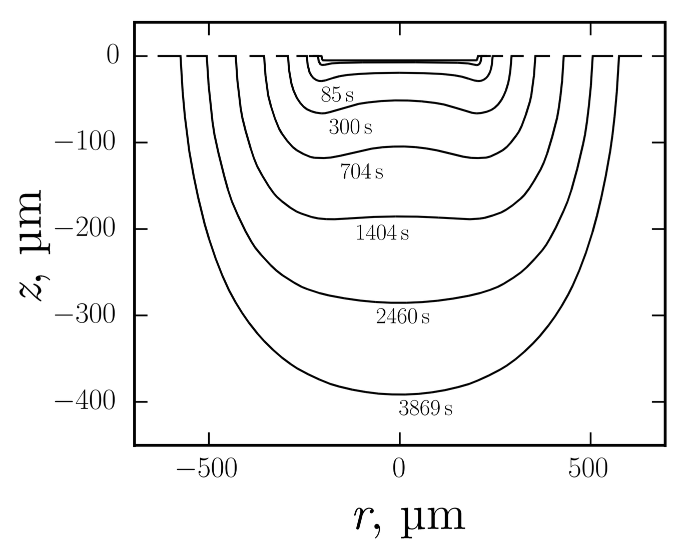
Alexey Ivanov[1], Ulrich Mescheder[1]

1. Furtwangen University, Institute for applied research, Robert-Gerwig-Platz 1, 78120 Furtwangen, Germany

Introduction: Electrochemical etching of silicon (anodization) in hydrofluoric acid (HF) can be applied for etching of well controlled 3D structures in silicon. In this work, etch form development observed in the anodization process through an insulating masking layer with a circular opening in galvanostatic regime was simulated in COMSOL and compared to experiment.



Schematic geometry of the model (not in scale) in 2D with axial symmetry



Simulated etch forms for diameter of opening 400 µm and initial current density of 1 A/cm²

Theory: For silicon anodization in HF-based electrolytes, with increase of current density, the process switches from divalent reaction of pore formation to tetravalent process of electropolishing.

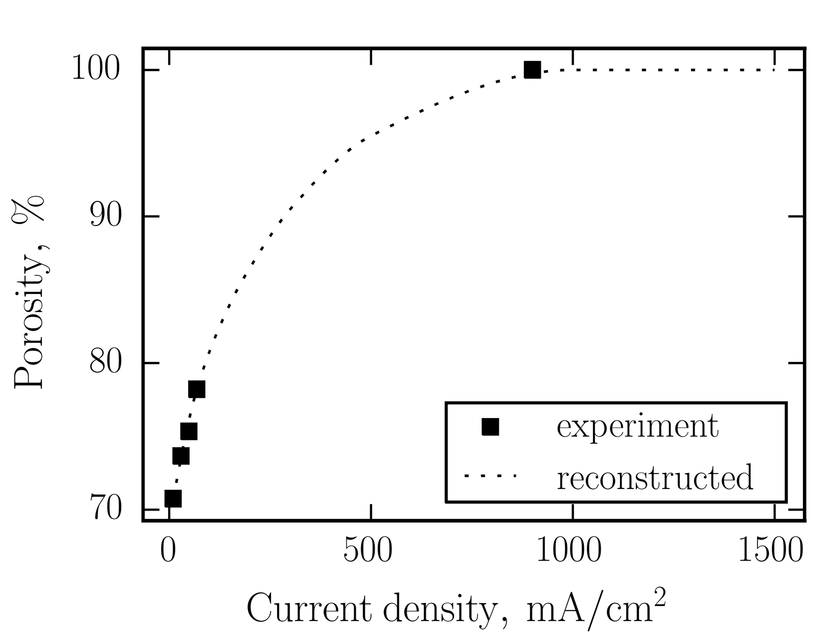
Amount of dissolved material and the dissolution rate is calculated from the Faraday's law of electrolysis with known current density j, dissolution valence n_e, porosity P, and density ρ_{Si} and molar mass M_{Si} of silicon:

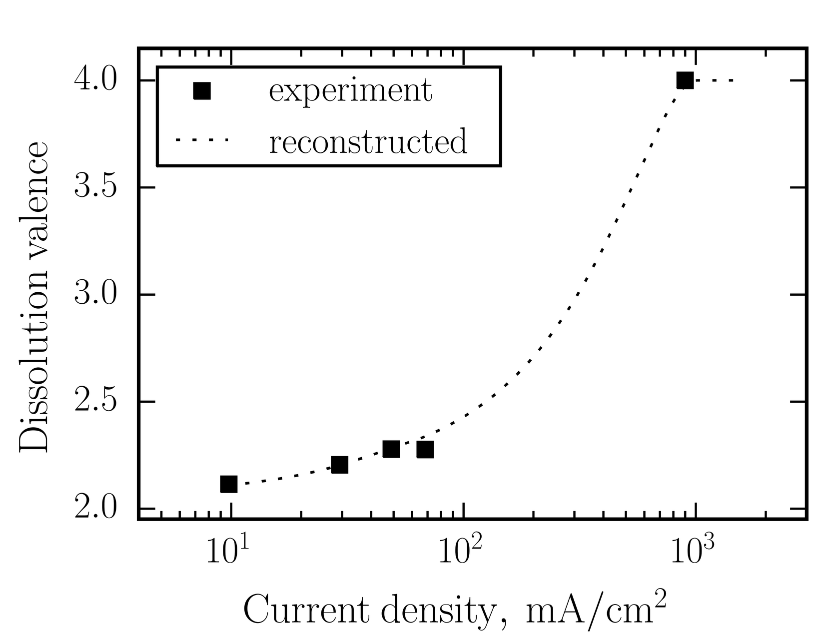
$$R = \frac{1}{P}\cdot\frac{j}{n_e e}\cdot\frac{M_{Si}}{\rho_{Si} N_A}$$

where e is the elementary charge and N_A is the Avogadro constant.

In the primary current distribution, only resistivity of the materials (electrodes, electrolyte) are taken into account, neglecting activation and concentration overpotentials.

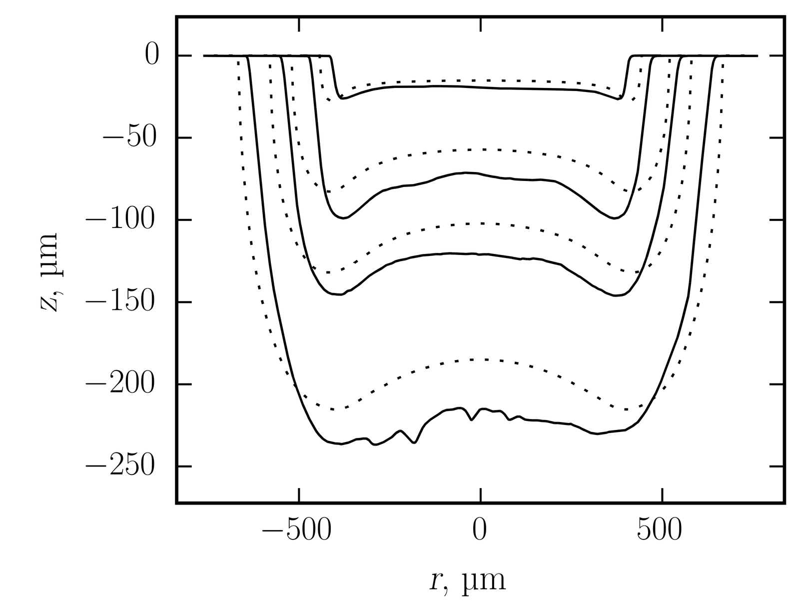
Experimental: For p-type silicon of resistivity in the range 10–20 Ω cm in the mixture of 50 m% HF and ethanol absolute in volume ratio 1:1, in the transition of the process from pore formation to electropolishing with increase of current density, valence n_e and porosity P of the generated porous silicon layer:



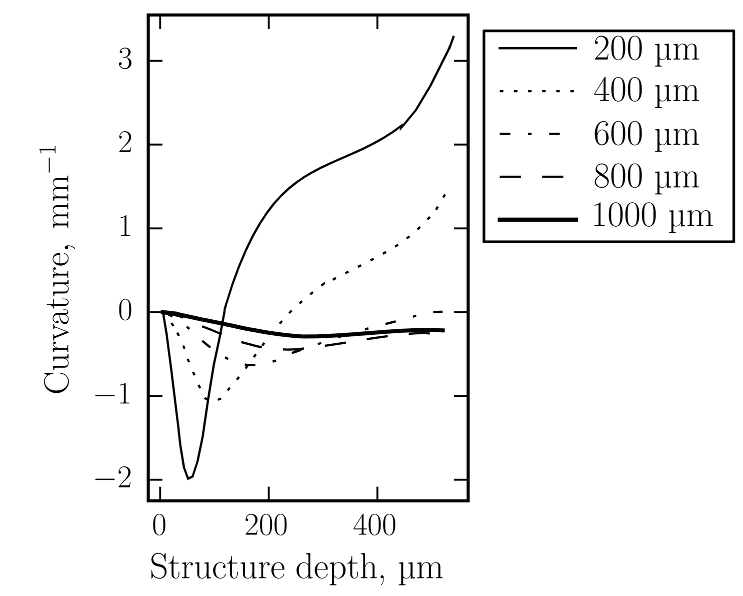


- Electrodeposition physics interface (*edsec*)
- Conductivities: 7.5 S/m (silicon) and 34.11 S/m (electrolyte)
- Opening diameter: [200, 400, 600, 800, 1000] µm
- Initial current density: [1.0, 1.5, 2.0, 2.5, 3.0, 3.5] A/cm²
- Etch time in the experiment: [1, 5, 10, 20] min
- In the experiment, multiple openings of all diameters on a sample with distance of 2 mm between the centers of openings

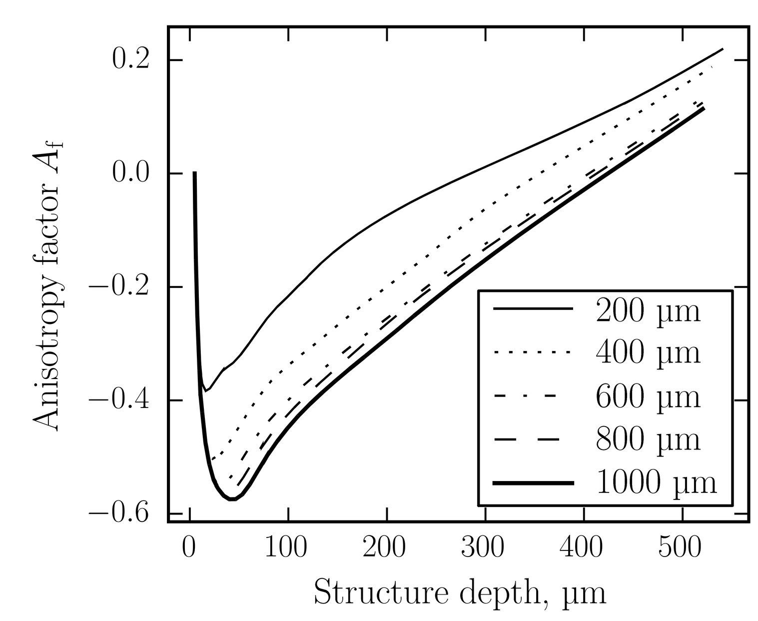
Results:

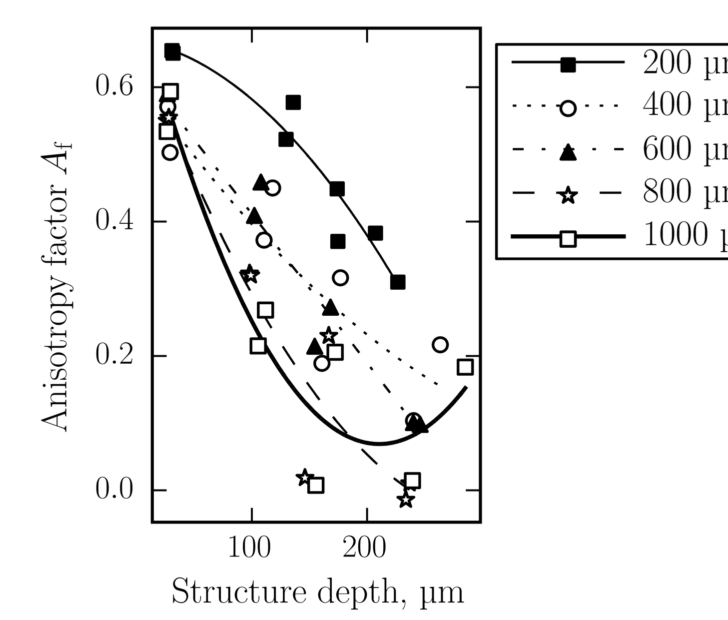


Simulated etch profiles (dotted lines) and experimental etch profiles (solid lines) for diameter of opening of 800 µm, initial current density of 1 A/cm² and etch time of 1 min, 5 min, 10 min, and 20 min.

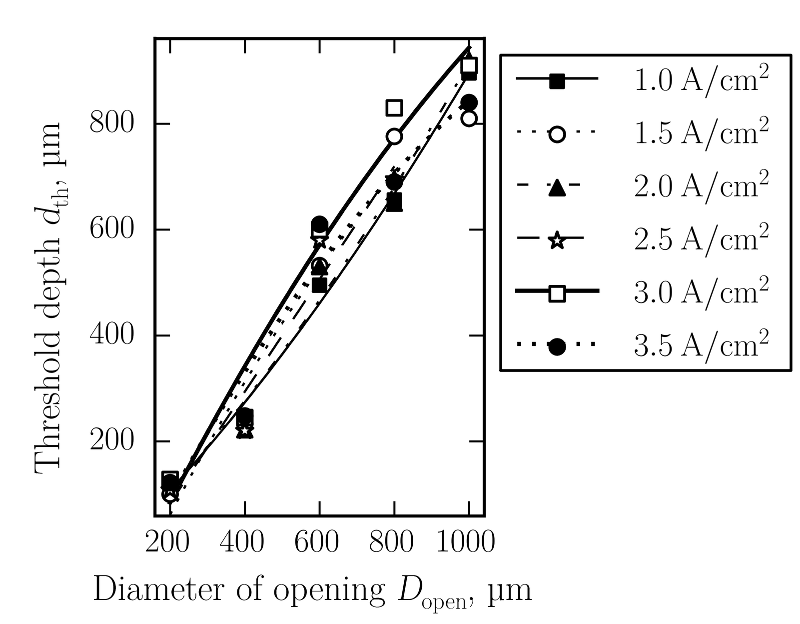


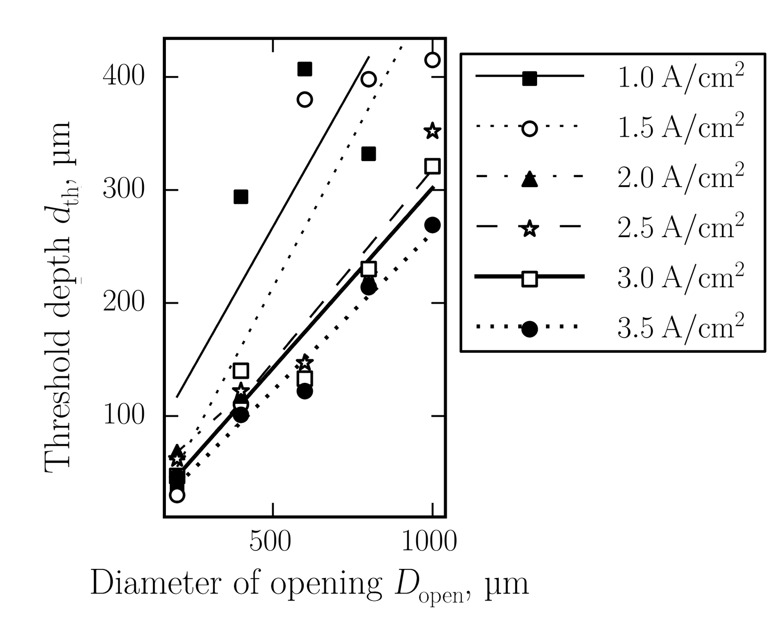
Curvature vs. structure depth for simulated etch forms for initial current density of 1 A/cm²; the values in the keys are opening diameter. Similar curves were obtained for all initial current densities in the model.





Anisotropy factor vs. structure depth for initial current density of 1 A/cm² for (left) simulated etch forms and (right) experimental etch forms; the values in the keys are opening diameter. In the simulation, similar curves for all applied initial current densities were obtained. In the experiment, with increase of initial current density, the slope decreased, and for initial current density of 3.5 A/cm2 anisotropy factor remained at large positive values of 0.4–0.7.





Threshold depth (at which shape transforms from convex to concave) vs. diameter of opening evaluated for (left) simulated data and (right) experimental data; the datasets are for varied initial current density; the values of threshold depth above 500 µm for the model were obtained by extrapolation of the curvature curves.

Conclusions:

- Model for silicon anodization, accounting for current density dependent dissolution valence and porosity, thus working in pore formation and electropolishing regimes, was developed.
- Transformation of etch forms from convex to concave was observed in the experiment and the model.
- Threshold depth values in the simulation were approximately twice larger than in the experiment, which is assumed to be the result of the model lacking the activation and concentration polarization.
- Much lower values of anisotropy obtained for the simulated etch forms are assumed to be the result of some other not considered factors, for example, dependence of the process on crystallographic orientation.