Simulation of Electrochemical Etching of Silicon with COMSOL

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Abstract: In the presented work the simulation of a silicon anodization process is performed. Two mechanisms of convex etch form development (diffusion in electrolyte, current flow) are proposed and simulated. Limitations of the developed models are discussed. Further work on improvement of the models is suggested.

Keywords: silicon, electrochemical etching, anodization.

1. Introduction

Electrochemical etching of silicon (anodization) in hydrofluoric acid (HF) is a flexible process that can be applied for etching of well controlled three-dimensional (3D) structures in silicon [1]. Porous silicon (PS), formed under specific conditions during the process, due to its extremely high inner surface can be removed selectively in a weak KOH solution. Therefore it is very suitable as a sacrificial layer for fabrication of different complex structures for micro-electro-mechanical systems (MEMS). An electropolishing mode of the process can be applied within the process in order to achieve high-quality surfaces (Fig. 1).

Reason for the difficulty of applying the process for mass production is the multitude of parameters influencing the process, such as electrolyte concentration and temperature, silicon substrate doping and type, and so on [2]. In order to evaluate the influence of these and other parameters on the process (separately and combined), development of a detailed model is necessary. COMSOL as an FEM simulation tool is very suitable for modeling of such a complicated multiphysical process as anodization. In the presented work the so called edge effect of the anodization process, which results in higher etching rate near the edges of structures and the formation of a convex etch form, will be modeled.

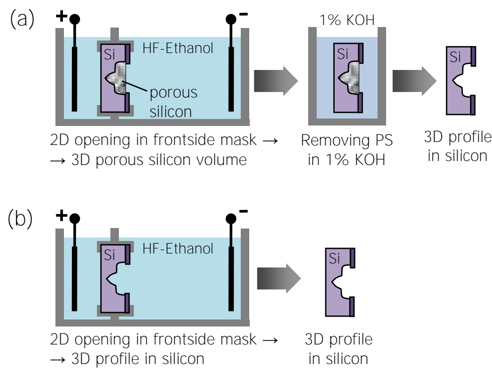


Figure 1. Process flow for structuring of silicon wafer with anodization process: (a) with porous silicon formation and (b) with electropolishing.

2. Anodization process

2.1 Process mechanism

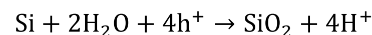
Silicon is stable in a HF solution, and etching is only running with supply of positive charges (holes) from the silicon substrate. The process is conducted in a HF stable tank with two platinum electrodes (Fig. 1).

There are two mechanisms of electrochemical etching of silicon in a HF electrolyte depending on the applied current density and HF concentration [3]. At low current density (low supply of holes) and high HF concentration (high supply of fluoride-ions) silicon atoms are directly dissolved with consumption of two holes per silicon atom (e.g. with reaction valence of 2) [2]:

$$Si + 4HF_2^- + h^+ \rightarrow SiF_6^{2-} + 2HF + H_2 + e^-$$

In this mode silicon atoms are dissolved selectively from the silicon substrate, this way pores of various shapes are etched into silicon, and porous silicon is formed. The skeleton of porous silicon remains crystalline [2].

At higher current densities (higher supply of holes from silicon) and lower HF concentration in the electrolyte (lower supply of fluoride-ions), the mechanism of silicon dissolution has two steps [2]. In the first step anodic oxidation takes place under the supply of four holes per silicon atom:



$$Si + 2H_2O + 4h^+ \rightarrow SiO_2 + 4H^+$$

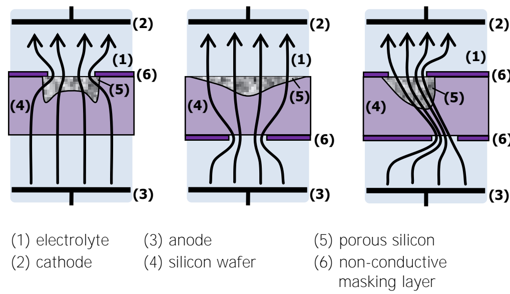


Figure 2. Schematic cross-sections of different principles of shape control during an anodization with adjustment of current flow through the silicon wafer by front- and back-side structuring of the wafer.

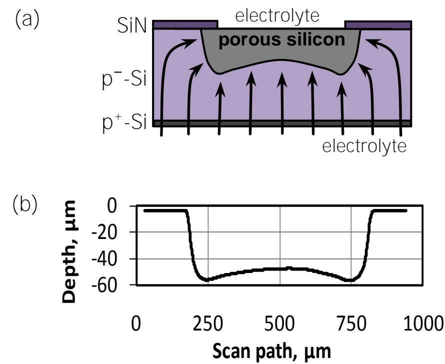


Figure 3. Edge effect in silicon anodization process: (a) schematic cross-section of a silicon sample, arrows represent current flow; (b) profile of a structure anodized through a 600 µm circular opening in a SiN masking layer in 30 wt.% HF at 2.5 A/cm² for t_{etch} = 1 min; measured with a stylus profiler.

The second step runs without consumption of positive charges from the substrate and consists of a silicon oxide dissolution in HF:

$$SiO_2 + 2HF_2^- + 2HF \rightarrow SiF_6^{2-} + 2H_2O$$

Thus, dissolution of silicon in electropolishing mode runs with a reaction valence of 4.

2.2 Shape control

Since the anodization process reactions require a supply of positive charges from the substrate, the local anodization rate is proportional to the current density. Thus the shape of the structure to be etched into a silicon substrate can be controlled by adjusting the local current flow with single- or double-side masking and/or local doping regions (Fig. 2) [1].

2.3 Experiments

The current flow through a p-type silicon (p-Si) sample with frontside stress-free silicon nitride (SiN) masking layer is schematically shown in Fig. 3a. The backside of the lowly doped silicon wafer forms a reverse-biased Schottky contact to the electrolyte. In order to provide an electrical (ohmic) contact, the backside of the whole wafer should be highly p-doped. The p-Si samples (10-20 Ohm-cm, (100)-Si, thickness ca. 520 µm) have been anodized in a double-tank cell configuration in in 30 wt.% HF with a current density of 2.5 A/cm².

For this case of an insulating front side masking, in the beginning of the process there is a higher etch rate near the edges of the mask, and a so called edge-effect (convex) shape is etched (Fig. 3b).

Two mechanisms are proposed for this edge effect. First, the specific current density distribution in silicon provides for the formation of a convex shape at the beginning of the process, because the current flow at structural edges (to masking layer) is considerably larger than the flow in the center of the opening (Fig. 4a).

A second mechanism which can explain the edge effect is based on the consideration of ion transport in the electrolyte in case of a

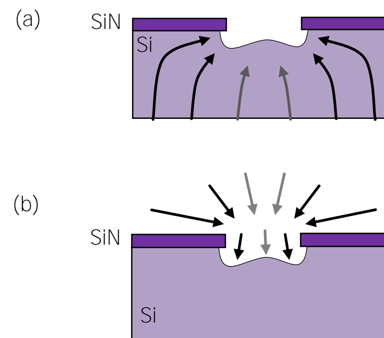


Figure 4. Simplified mechanisms of an edge effect: (a) effect of current distribution (arrows represent current flow); (b) effect of diffusion-controlled etching process (arrows represent the flow of F-ions to the reaction site); darker arrows indicate stronger flow.

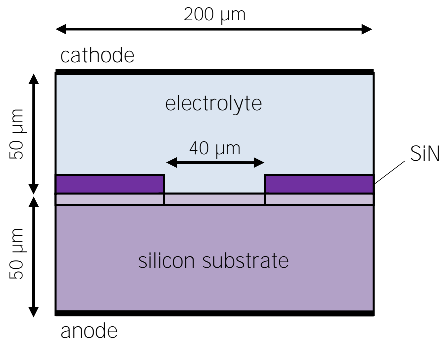


Figure 5. Schematic geometry of the model (not in scale).

Table 1: Material properties of the domains in the electrical model

Domain	Electrical conductivity	Relative permittivity
Electrolyte	1e4 [S/m]*	80.1
Silicon	10 [S/m]	11.1
Silicon nitride	0 [S/m]	7.5

* Value of the electrolyte electrical conductivity is to be verified in further work.

diffusion-controlled etching process: the resulting concentration of reacting ions is then critically depending on geometry (mask thickness, opening dimensions) and can provide for an edge effect as known from wet chemical etching [4] (Fig. 4b).

3. Simulation of edge effect

3.1 General considerations

Both mechanisms of the edge effect mentioned in the previous section appear to play a role to different extent depending on the applied current, electrolyte concentration, etc.

The first step on the way to a full model of the anodization process is to simulate the electrical and diffusion mechanisms separately, and the respective models are presented in this section below.

Both, the electrical and the diffusion models have been simulated in 2D. The geometry of the models is equal and consists of the following domains (Fig. 5):

- electrolyte;
- silicon substrate;
- insulating SiN layer (thickness 200 nm) on the silicon substrate with an opening of width 40 µm;
- thin 100nm layer under the SiN layer and under the electrolyte for enhanced mesh movement; this layer belongs to the silicon substrate material domain.

The movement of the etch front was implemented with deformed geometry interface (dg), where free deformation for all domains except SiN domains has been applied. SiN domains have been fixed.

3.2 Electrical model

The Electric Currents (ec) physics interface has been applied to all domains for simulation of the current flow in the model. The parameters defined for the domains are summarized in Table 1.

For the boundary between the electrolyte and the silicon substrate domains (etch front), a prescribed mesh velocity is defined as following:

$$\upsilon_x = -K_E \cdot j_x$$

$$\upsilon_y = -K_E \cdot j_y$$

where j_x and j_y are x and y components of the current density vector, and K_E is a coefficient of proportionality for the electrical model. If we assume electropolishing mode, i.e. no porous silicon formation, than

$$K_E = \frac{1}{z \cdot e} \cdot \frac{M_{Si}}{\rho_{Si} \cdot N_A}$$

where z is a reaction valence, e is the elementary charge, M_{Si} is the silicon molar mass, ρ is the silicon density and N_A is the Avogadro constant. For the reaction valence of 4:

$$K_E = 3{,}1234 \cdot 10^{-11} \, \frac{\mathrm{m}^3}{\mathrm{A} \cdot \mathrm{s}}$$

The upper boundary of the electrolyte (cathode) was grounded. To the lower boundary of the silicon substrate (anode) an electrical potential of 1V has been applied.

The resulting etch form after 0.3 s of anodization process is shown in Fig.6 and Fig.7.

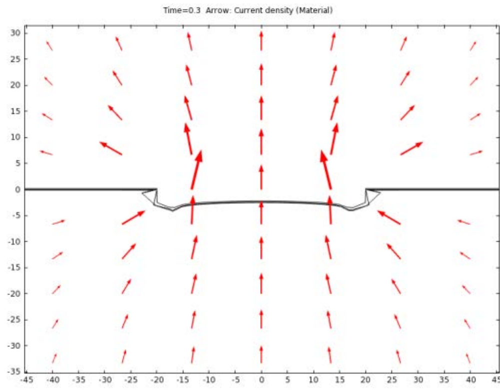


Figure 6. Resulting etch form after 0.3 s of anodization process for the electrical model. Arrows represent the current density flow.

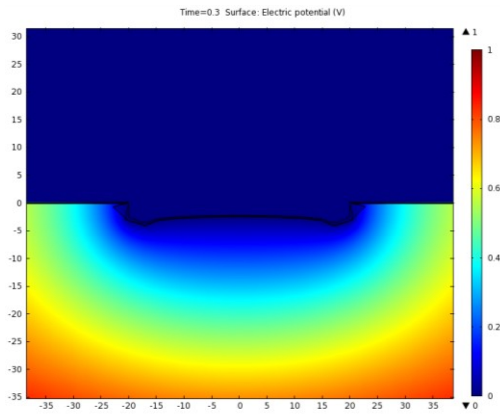


Figure 7. Electric potential distribution after 0.3 s of anodization process for the electrical model.

3.3 Diffusion model

The Transport of Diluted Species (chds) physics interface has been applied for the simulation of diffusion in electrolyte.

The following parameters have been used in the model:

- electrolyte initial concentration

$$c_0 = 5.7483\ \mathrm{M}$$

- diffusion coefficient for HF and HF_2^- [5]

$$D = 3 \cdot 10^{-9}\ \mathrm{m^2/s}$$

- assumed order of reaction: 1st order
- assumed reaction rate constant $k = 1\ \mathrm{m/s}$
- reaction rate variable defined for the boundary between electrolyte and the silicon substrate for the 1st order reaction:

$$R = k \cdot c$$

For the boundary between the electrolyte and the silicon substrate domains (etch front), a prescribed mesh velocity is defined as follows:

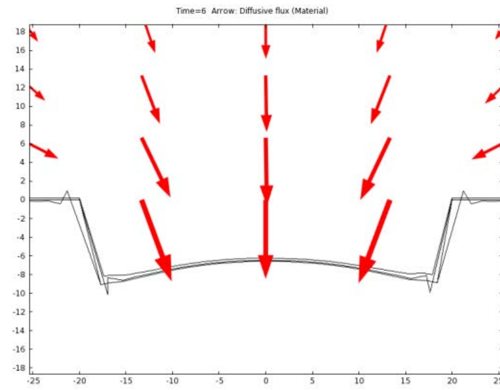


Figure 8. Resulting etch form after 6 s of anodization process for the diffusion model. Arrows represent a diffusive flux.

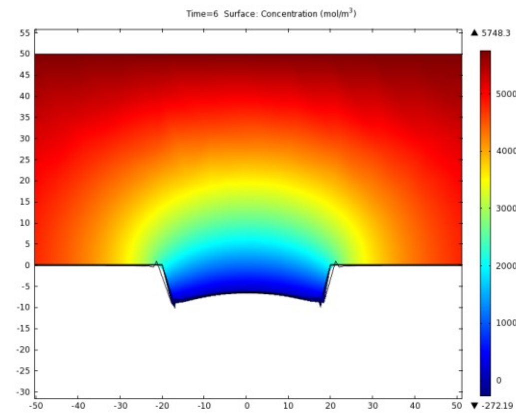


Figure 9. Concentration distribution after 6 s of anodization process for the diffusion model.

$$v_x = R \cdot K_D \cdot chds.nx$$

$$v_y = R \cdot K_D \cdot chds.ny$$

where K_D is a coefficient of proportionality for the diffusion model:

$$K_D = \frac{M_{Si}}{m \cdot \rho_{Si}}$$

where m is a stochiometric reaction parameter. For $m = 6$ (reaction of oxide etching):

$$K_D = 2{,}01 \cdot 10^{-6}\ \frac{\mathrm{m^3}}{\mathrm{mol}}$$

For the boundary between the electrolyte and the silicon substrate, an inward flux equal to $-R$ has been defined. For the left side, right side and top boundaries of the electrolyte the concentration was fixed to c_0.

The resulting etch form for the diffusion model is shown in Fig. 8 and Fig. 9.

It should be noted, that simulation of the diffusion process and of its influence on the etch form presented here was done for demonstration purposes only, therefore some assumptions and values of parameters have to be verified for the simulation of a real process.

4. Discussion

Etch forms obtained for the models have demonstrated the edge effect mechanisms. However, there are some improvements needed for the models.

First, the chosen geometry and the mesh are not very accurate. Improvements of mesh and geometry and application of remeshing can help to solve for deeper etch forms and demonstrate further development of the edge effect and the transformation of convex edge effect etch forms into concave as was observed experimentally [1].

The diffusion model considers only diffusion transport in electrolyte. However, there are other transport phenomena in the process such as convection and drift, and their influence on etch form should be evaluated in further work.

The parameters used in the diffusion model need to be verified. For example, a 1st order reaction has been simulated for simplicity, however, in the electropolishing mode of the anodization process the limiting reaction is silicon dioxide etching, and this reaction is of higher order [5].

5. Conclusions

In this paper models for the simulation of the edge effect in silicon anodization processes have been presented. Final goal of the work is to have a complete model of the silicon anodization process. In future work the influence of other parameters on the process will be studied, such as porous silicon layer formation during the process, evolution of hydrogen bubbles at the reaction site, heat, switching between the porous silicon formation mechanism and electropolishing and so on.

6. References

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7. Acknowledgements

The presented work is a part of PhD research performed at the Furtwangen University in cooperation with the University of Freiburg and supervised by Prof. Dr. Peter Woias (University of Freiburg, IMTEK) and Prof. Dr. Ulrich Mescheder (Furtwangen University). Dr. Rolf Huster (Furtwangen University) is acknowledged for some valuable remarks on the paper.