Dynamic Simulation of Electrochemical Etching of Silicon

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Abstract: In the presented work the dynamic simulation of a silicon anodization process is performed. Two mechanisms of etch form development (diffusion in electrolyte, current flow) are considered and simulated. Influence of electrolyte conductivity and radius of the opening in the masking layer is discussed.

Keywords: silicon, electrochemical etching, anodization, 3D etching.

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 surface quality even for optical applications (roughness in the order of nm) (Fig. 1).

Up to now application of the process for mass production is hindered due to 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 development of etch form during the process will be modeled. The paper introduces further development of the models since the previous publication [3].

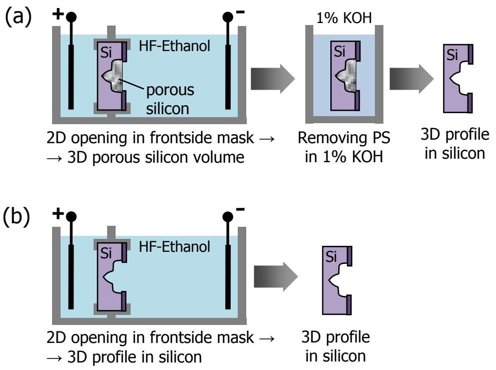

Figure 1. Process flow for structuring of silicon wafer with anodization process: (a) with porous silicon formation and (b) with electropolishing.

2. Anodization process

2.1 Process mechanism

Etching of silicon in HF 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 [4]. 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]:

$$\mathrm{Si} + 4\mathrm{HF}_2^- + \mathrm{h}^+ \rightarrow \mathrm{SiF}_6^{2-} + 2\mathrm{HF} + \mathrm{H}_2 + \mathrm{e}^-$$

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

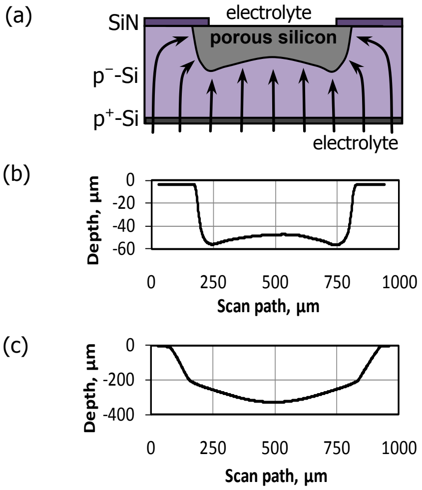

Figure 2. Etch form development in silicon anodization process: (a) schematic cross-section of a silicon sample, arrows represent current flow; (b, c) profile of a structure anodized through a 600 µm circular opening in a SiN masking layer in 30 wt.% HF at 2.5 A/cm² for (b) t_{etch} = 1 min and (c) t_{etch} = 10 min; measured with a stylus profiler; straight regions on both sides of the concave profile are measurement artifacts.

place under the supply of four holes per silicon atom:

$$\mathrm{Si} + 2\mathrm{H_2O} + 4\mathrm{h^+} \rightarrow \mathrm{SiO_2} + 4\mathrm{H^+} \qquad (1)$$

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

$$\mathrm{SiO_2} + 2\mathrm{HF_2^-} + 2\mathrm{HF} \rightarrow \mathrm{SiF_6^{2-}} + 2\mathrm{H_2O} \qquad (2)$$

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

2.2 Etch form development

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. 2a. The backside of the low 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 30 wt.% HF with a current density of 2.5 A/cm².

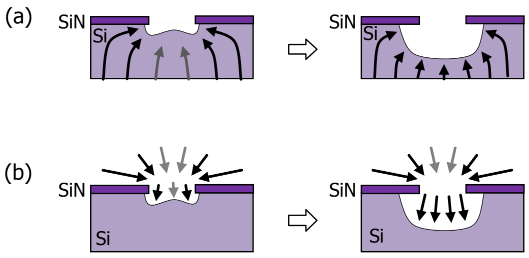

Figure 3. Simplified mechanisms of etch form transformation convex-concave during anodization process: (a) effect of current distribution (arrows represent current flow); (b) effect of diffusion-controlled etching process (arrows represent the flow of F-ions to the reaction site); darker arrows indicate stronger flow.

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. 2b). At longer etching time, etch form transformation from convex to concave has been observed in the experiments.

Two mechanisms are proposed to have effect on such shape development. First, the specific current density distribution in silicon provides formation of convex shape at the beginning of the process because of current concentration at the edge (larger current flow at the edge than in the center of structure, Fig. 3a left). Assuming a similar conductivity of electrolyte and silicon substrate, etching deeper into the substrate will lead to formation of more concave shape (Fig. 3a right).

From the other side, the shape conversion can be provided with ions transport in the electrolyte in case of diffusion-controlled etching process. The resulting concentration of reacting ions is then critically depending on geometry (mask thickness, opening dimensions) and thus will change during the etching, which will convert the etch shape from convex to concave (isotropic) as known for wet chemical etching [5] (Fig. 3b).

3. Simulation of anodization process

3.1 General considerations

Both mechanisms of the shape transformation 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.

For both cases the models have been simulated in 2D with axial symmetry. The geometry of the models consists of the following domains (Fig. 4):

- electrolyte;
- silicon substrate;
- insulating SiN layer of thickness 1 µm on the silicon substrate with an opening of varied radius x in the range 20 µm – 500 µm;
- "predefined etch form" of thickness 1 µm for enhanced mesh movement; this domain belongs to the electrolyte region.

The movement of the etch front was implemented with *moving mesh interface* (ale), where free deformation for the silicon substrate and "predefined etch from" domains has been applied. In order to simulate properly lateral etching (mask underetching), geometry finalization method *assembly* with generation of *identity pairs* of elements in a boundary of two neighbouring mesh domains was applied. A further enhancement of the simulation process for deep etch form was achieved with application of automatic remeshing function available in COMSOL starting from the version 4.2. The simulation was performed in COMSOL 4.2a.

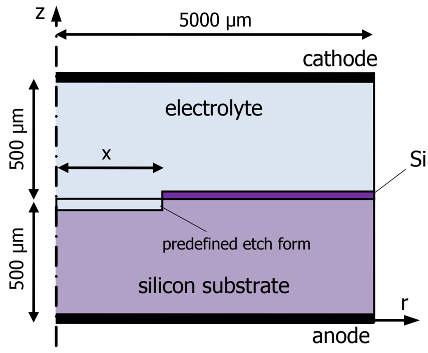

Figure 4. Schematic geometry of the model (not in scale) in cylindrical coordinates; opening radius x varied.

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. Etch front movement for two values of electrolyte conductivity was simulated. The parameters defined for the domains are summarized in Table 1. For the boundary between the initial etched region and the silicon substrate (etch front), a *prescribed mesh velocity* in cylindrical coordinates is defined as following:

$$\upsilon_r = -K_E \cdot j_r \tag{3}$$

$$\upsilon_z = -K_E \cdot j_z \tag{4}$$

where j_r and j_z are r and z components of the current density vector, and K_E is a constant for the electrical model, which takes into account silicon density, reaction valence, etc. If we assume electropolishing mode, i.e. no porous silicon formation, than

$$K_E = \frac{1}{z \cdot e} \cdot \frac{M_{Si}}{\rho_{Si} \cdot N_A} \tag{5}$$

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

$$K_E = 3{,}1234 \cdot 10^{-11}\ \frac{\mathrm{m}^3}{\mathrm{A \cdot s}} \tag{6}$$

Electric potential of 1 V was applied to the anode. The cathode was grounded.

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

Domain	Electrical conductivity [S/m]	Relative permittivity
Electrolyte	$\sigma_{el.1} = 10^4$ $\sigma_{el.2} = 10$	80.1
Silicon	$\sigma_{Si} = 10$	11.1
Silicon nitride	0	7.5

As an example, the resulting etch forms for two different values of diameter of the opening in the masking SiN layer (200 µm and 1000 µm) are shown in Fig. 5 (electrolyte conductivity $\sigma_{el.1}$) are Fig. 7 (electrolyte conductivity $\sigma_{el.2}$). Corresponding current and potential distributions for the models with the diameter of the opening 1000 µm for $\sigma_{el.1}$ and $\sigma_{el.2}$ are shown in Fig. 6 and Fig. 8.

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:

- initial electrolyte concentration

$$c_0 = 5.7483\ \mathrm{M} \tag{7}$$

- diffusion coefficient for HF and HF_2^- [6]

$$D = 3 \cdot 10^{-9}\ \mathrm{m^2/s} \tag{8}$$

- assumed order of reaction: 1st order
- assumed reaction rate constant $k = 1\ \mathrm{m/s}$ to provide diffusion-controlled process [5]
- reaction rate variable defined for the boundary between electrolyte and the silicon substrate for the 1st order reaction:

$$R = k \cdot c \tag{9}$$

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

$$v_r = R \cdot K_D \cdot n_r \tag{10}$$

$$v_z = R \cdot K_D \cdot n_z \tag{11}$$

Where n_r and n_z are normal vectors, and K_D is a constant for the diffusion model:

$$K_D = \frac{M_{Si}}{m \cdot \rho_{Si}} \tag{12}$$

where m is a number of Fluor atoms needed for dissolution of one atom of silicon. In the electropolishing mode, six atoms of Fluor are required in the reaction of silicon dioxide dissolution (Equation (2)). Then:

$$K_D = 2{,}01 \cdot 10^{-6}\ \frac{\mathrm{m^3}}{\mathrm{mol}} \tag{13}$$

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.

For all diameters of the opening in the SiN masking layer, formation of convex shape in the beginning with transformation to concave shape was observed. As an example, the resulting etch forms and concentration distributions for the diffusion models with diameter of the opening in the masking SiN layer 40 µm and 800 µm are shown in 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

With both electrical and diffusion models the transformation of etch form convex-concave has been demonstrated.

For the electrical model, in the electrolytes with both conductivities $\sigma_{el.1}$ and $\sigma_{el.2}$ in the beginning of the process there is higher current flowing near the edges of the SiN masking layer, which leads to the formation of convex edge effect etch form. However, there is a difference in further development of etch shapes. In highly conductive electrolyte, deeper parts of the etch form at the edges of the opening lead to further increase of current to these regions due to lower resistance (these regions are filled with highly conductive electrolyte), and this way the edge effect is self amplifying (Fig. 5). This self-amplification is well demonstrated with electric potential distribution and current flow figures (Fig. 6 right).

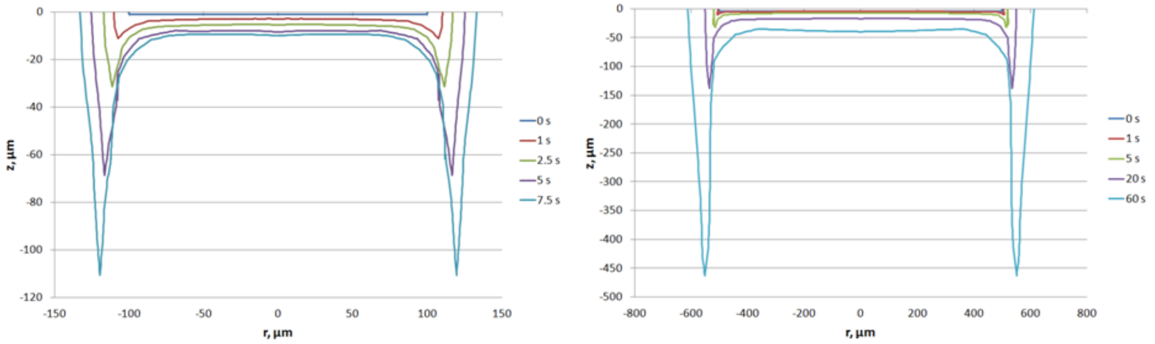

Figure 5. Resulting etch forms of anodization process for the electrical models with the electrolyte conductivity $\sigma_{el.1}$ and diameter of the opening in SiN masking layer 200 µm (left) and 1000 µm (right)

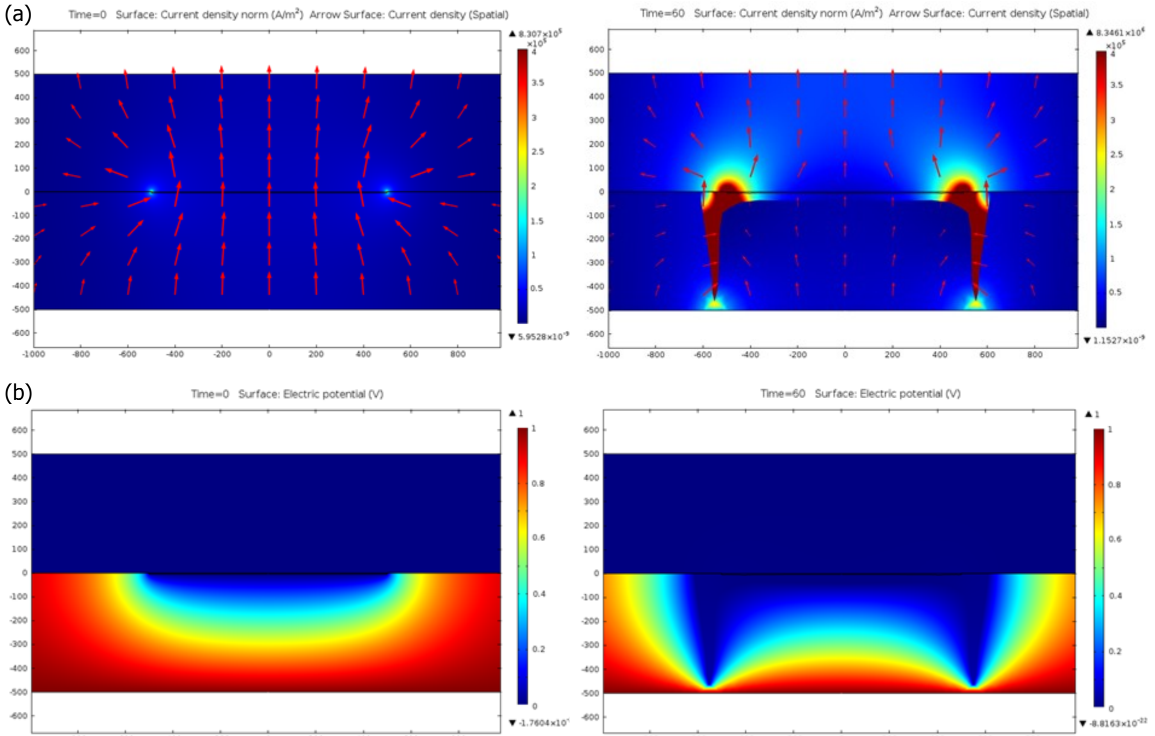

Figure 6. (a) current density and (b) potential distribution for the electrical model with the electrolyte conductivity $\sigma_{el.1}$ and diameter of the opening in SiN masking layer 1000 µm at 0s (left) and 60s (right) of the anodization process. Arrows on the current density distribution plots represent the current density flow.

In contrast, in the electrolyte with low conductivity convex form transforms into concave during the anodization process (Fig. 7). Similar results have been observed before in electrical simulation performed with other FEM software [7]. Electric potential and current density distributions are shown in Fig. 8.

In the diffusion model with the defined parameters for diffusion controlled etching process, typical etch form development was observed, with form conversion from convex (edge effect) to concave (isotropic) (Fig. 9a).

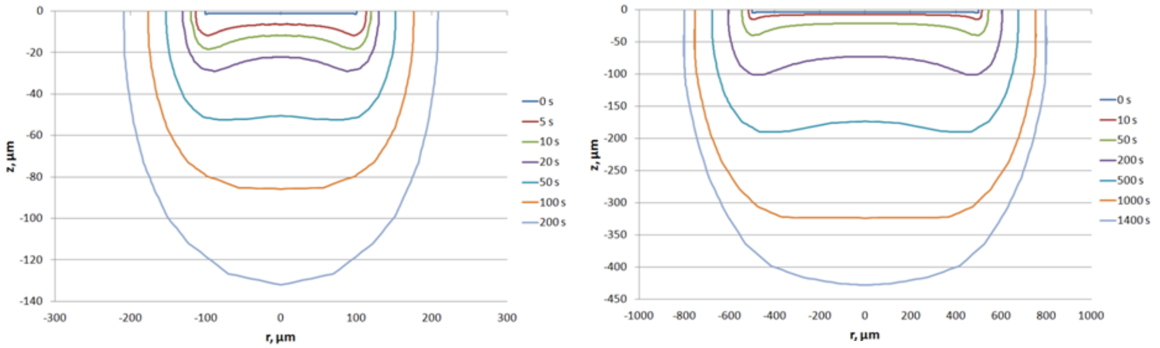

Figure 7. Resulting etch forms of anodization process for the electrical models with the electrolyte conductivity $\sigma_{el.2}$ and diameter of the opening in SiN masking layer 200 µm (left) and 1000 µm (right)

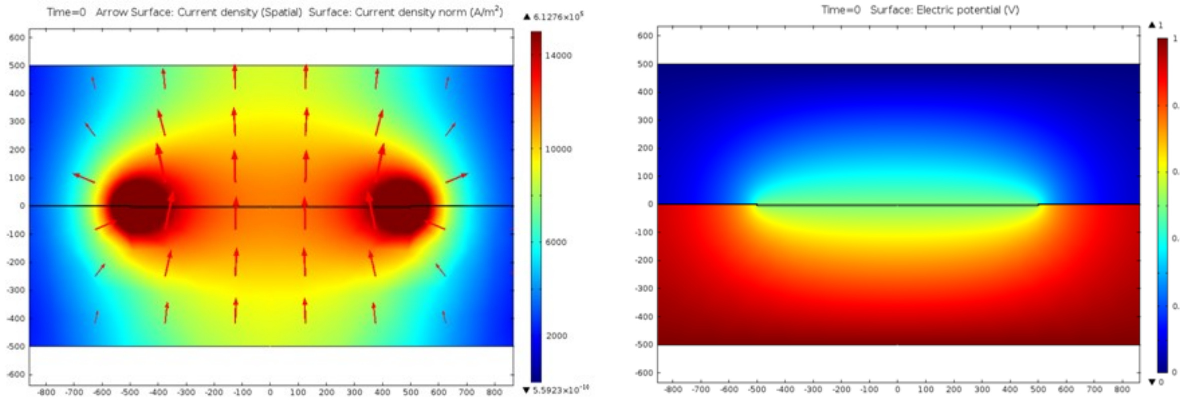

Figure 8. Current density (left) and potential distribution (right) for the electrical model with the electrolyte conductivity $\sigma_{el.2}$ and diameter of the opening in SiN masking layer 1000 µm at the beginning of the anodization process. Arrows on the current density distribution plots represent the current density flow. The distributions for the end of the process are identical and therefore not shown.

Due to diffusion limitation, concave isotropic form is achieved when the distance from the opening in the masking layer to the etch front gets comparable to the diameter of the opening (approximately 25%-35% for the simulated diameters of the opening). For the diameter of the opening 40 µm this happened at depth ca. 10.5 µm and for 800 µm at depth ca. 276 µm. Further supply of chemical species to the reaction site through the opening in the masking layer after this depth can be considered as a supply from a point source, equally distant from all the points of the etch front, which provides uniform etch rate along the etch front, as can be observed on the concentration distribution plot (Fig. 9b right).

It is important to note, that 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 have 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 [6].

5. Conclusions

In this paper models for the dynamic simulation of etch front in silicon anodization processes have been presented. Final goal of the ongoing work is to have a complete model of the silicon anodization process. In future work the presented results will be compared to the experiments, and the influence of other parameters on the process will be studied, such

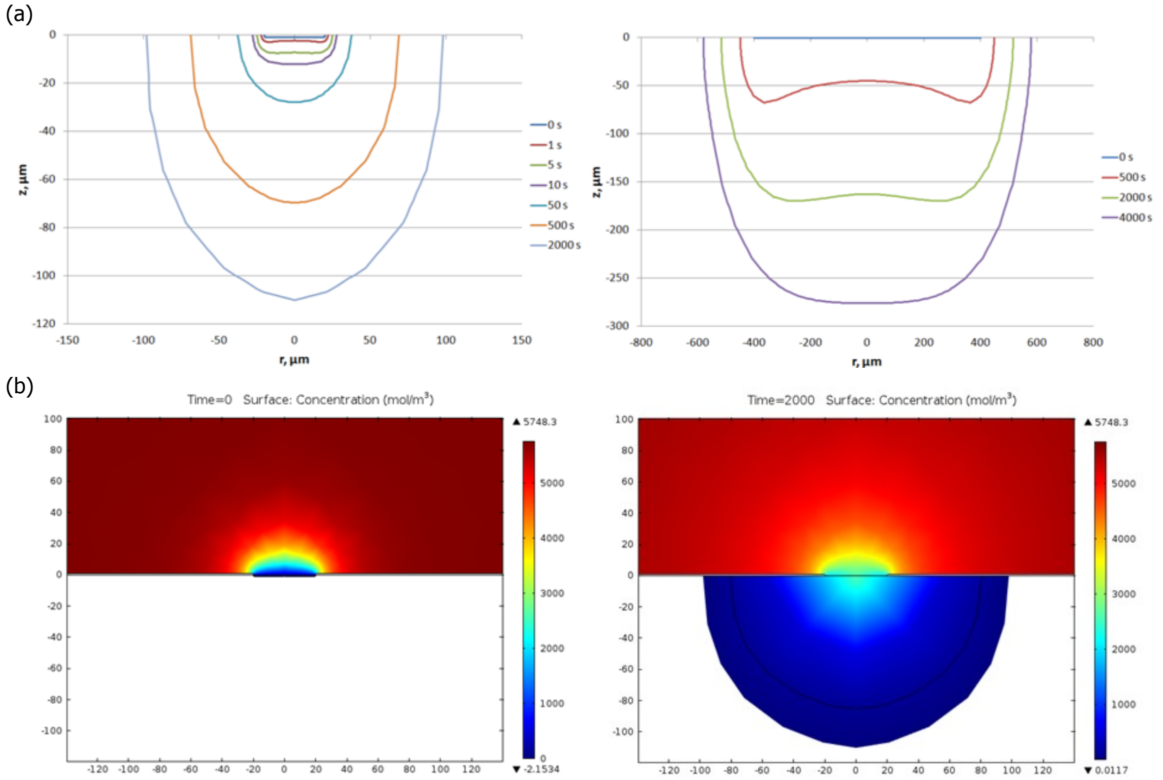

Figure 9. (a) Resulting etch forms of anodization process for the diffusion models with diameter of the opening in SiN masking layer 40 µm (left) and 800 µm (right); (b) concentration distributions at the beginning (left) and after 2000 s (right) of the process for the model with the diameter of the opening 40 µm.

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 in frames of the project #94 µECM (Era.Net RUS) 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).