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Finite-elements simulation of etch front propagation in silicon electropolishing process

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Electrochemical etching of silicon (anodization) in hydrofluoric acid (HF) is a flexible process that can be applied for etching 3D structures in silicon with controlled anisotropy [1]. At low applied current densities and high concentration of HF in electrolyte, porous silicon (PS) is formed. At higher current densities and low HF concentrations the etch process runs in diffusion controlled mode through oxide formation, and silicon wafer surface is electropolished. In the presented work electrochemical axisymmetrical 2D FEM model for simulation of etch front movement during the electropolishing process for the first time has been developed and verified experimentally.

In electropolishing mode the process of silicon etching runs in two steps [2]. In the first step anodic oxidation takes place under the supply of four electronic 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.

Net reaction regarding charge transfer and ionic reactants and products implemented in the model is the following:

$$\mathrm{Si} + 2\mathrm{HF_2^-} + 2\mathrm{HF} + 4\mathrm{h^+} \rightarrow \mathrm{SiF_6^{2-}} + 4\mathrm{H^+} \qquad (3)$$

For validation of the model, silicon substrate with frontside silicon nitride masking film has been considered (Fig. 1a). Reaction area has been defined with a circular opening of diameter 1 mm in silicon nitride. Experimental observations for such structure showed that during electropolishing etch shape undergoes specific changes [3]: in the beginning of the process a so called edge-effect is observed (convex shape due to higher etch rate near the edges of the mask) (Fig. 1b). At longer etching time, etch form transforms from convex to concave (Fig. 1c). Two mechanisms have been proposed to have effect on such shape development: effect of current flow though the interface silicon-electrolyte (Fig. 2) and effect of reactants' transport in electrolyte as known for wet-chemical etching in case of diffusion controlled process. Effect of both mechanisms on etch shape have been simulated in separate models previously [4, 5]. In the presented model for the first time both mechanisms are brought together to form a complete model of electrochemical etching of silicon on a macro scale (i.e. for simulation of etch front movement during the process).

Simulated etch form with a developing convex form is shown in Fig. 3. Comparison of the simulated and experimental results is discussed in the paper.

References

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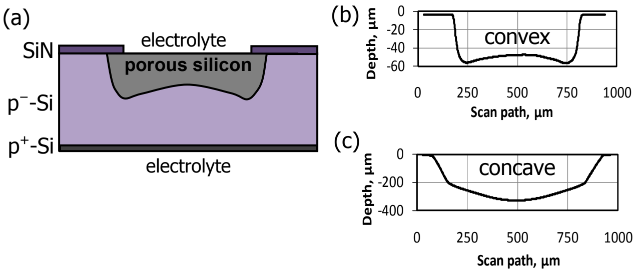

Figure 1. Etch form development in silicon anodization process: (a) schematic cross-section of a silicon sample; (b, c) experimental profile of a structure anodized through a 600 µm circular opening in a SiN masking layer in 30 wt.% HF at 2.5 A/cm² for (b) t_{etch} = 1 min and (c) t_{etch} = 10 min; measured with a stylus profiler.

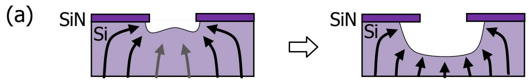

Figure 2. Simplified mechanism of etch form transformation convex-concave during anodization process as effect of current distribution; arrows represent current flow, darker arrows indicate stronger flow.

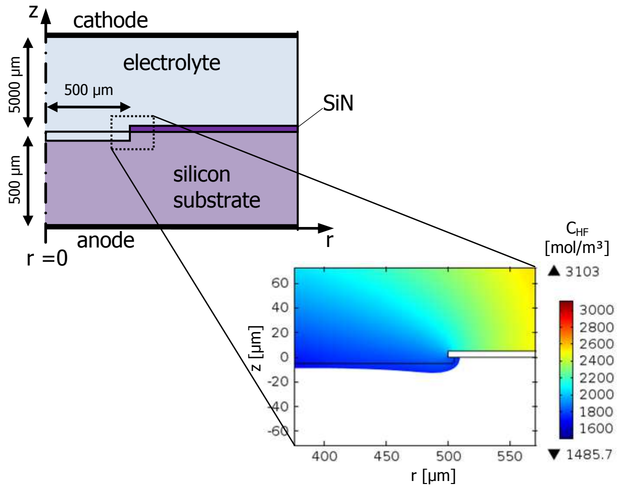

Figure 3. Top: geometry of the axisymmetrical 2D model; bottom: simulated concentration distribution of HF and etch form of convex shape (t_{etch} = 41s).