The process of pore formation on a textured silicon substrate during electrochemical etching: 3D model

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Abstract. The paper presents the results of modeling the mechanism for producing porous silicon on a textured surface. For various technological tasks, it is important to learn how to control the parameters of electrolytic etching to obtain the desired result. On 3D maps of the distribution of potential and etching currents, you can see that the vectors go around the pyramids and pointly etch certain sections of the surface. Confirmations of this can be seen in photographs of a scanning electron microscope and a scanning probe microscope. A detailed description of pore formation on textured porous silicon substrates has not yet been found in other works.

1. Introduction

The process of pore formation on a flat surface of single-crystal silicon during electrochemical etching is described in many models, which to some extent explain the physical laws of this phenomenon [1-5]. Most of the developed models of pore formation do not take into account the effect of the microrelief on the surface of the silicon wafer, where the anode-electrolyte interface is usually considered flat. In this paper, we consider the process of pore formation on a textured silicon surface and solve the problem of constructing a physical and mathematical model describing the field distribution in the electrolyte – nonplanar anode system. Structures with a porous layer formed on a textured surface are of particular interest for practical applications in optoelectronics, and the formation of pores on such a surface has its own characteristics that are not taken into account in existing models of pore formation [6, 7].

2. The method of sample production

A porous layer on the wafer surface was created by electrochemical etching in alcoholic solutions of hydrofluoric acid in vertical type electrochemical cells [6, 7]. On one side of the etched cell was a silicon wafer tightly pressed against a graphite contact acting as an anode, and on the other hand, to a graphite electrode acting as a cathode (Fig. 1). The initial surface of the plates was textured, i.e., covered with tetrahedral regular pyramids with a crystallographic orientation (100) [8], and not as an independent document. Please do not revise any of the current designations.
Figure 1. Scheme of electrolytic cell of horizontal type for formation of porous silicon layers.

3. Method of modeling

The distribution of the field strength in the electrolyte and at the silicon-electrolyte interface was simulated using the COMSOL Multiphysics software, namely, the module “Secondary current distribution” for the electrochemical cell. The charge transfer in the electrolyte was described by Ohm’s law. Two assumptions were suggested: firstly, the electrolyte is electrically neutral, and secondly, the change in the composition of the electrolyte is insignificant (uniform). It was also taken into account that when the electrode is in contact with the electrolyte solution, a space charge region is formed in the semiconductor, similar to the region formed when the semiconductor contacts the metal, which leads to a curvature of the energy zones of the semiconductor. The potential applied to the electrode is redistributed between the depleted semiconductor region and the Helmholtz layer. The main equation that was used to build the computer model was the Nernst – Planck equation for ion transport in an electrolyte.

The simulation was performed in COMSOL Multiphysics program for electrochemical cell. The initial conditions were as follows: the electrolyte is considered to be an electroneutral incompressible liquid, the change in the composition of which is negligible, there is no turbulence, P= 1 ATM, T=293K, the parameters ρ and μ – const. Before connecting an external current source, an electrode potential arises in the system, associated with the appearance of a double electric layer at the interface semiconductor-electrolyte. The dependence of the electrode potential on the concentration of cations in the solution and the temperature is described by the Nernst equation:

$$\varphi = \varphi^0 + \frac{RT}{nF} \ln \frac{a(\text{ox})}{a(\text{red})}$$

(1)

$\varphi^0$ - the standard electrode potential, n – the number of electrons involved in the reaction, F - Faraday constant, R - the universal gas constant, a(ox), and(red) – activity, respectively, oxidized and reducing forms.

When the system is connected to an external voltage source, the flow of current through the electrolytic bath begins, while ignoring the influence of the electrode kinetics, the potential difference at the boundary practically does not deviate from its equilibrium value. There is no activation overvoltage, therefore, the current distribution depends only on the geometry of the anode and cathode.
The dependence of the diffusion current on the concentration of ions and the electric field in the electrolyte - the Nernst-Planck equation:

\[ \mathbf{J}_m = -D \nabla c - U_m Z F c \nabla \phi \]  

(2)

\( J_m \) - ion mole flux density, mole\(^{-1}\)cm\(^2\); \( D \) - diffusion coefficient, cm\(^2\)c\(^{-1}\); \( c \) - ion concentration, mole cm\(^{-3}\); \( U_m \) - ion mobility for mole (\( U_m = D/RT \)); cm\(^2\) mole\(^{-1}\)C\(^{-1}\); Z - charge number, F- Faraday constant, C mol\(^{-1}\). (\( F = eN_a \)), the field strength is expressed in terms of the potential gradient.

The current density in the electrolyte:

\[ \mathbf{j} = -\delta_i \nabla \phi \]  

(3)

Current density on the electrode:

\[ \mathbf{j} = -\delta_s \nabla \phi \]  

(4)

\( \delta_i, \delta_s \) - conductivity of the substance specified in the model.

4. Results and discussions

The calculation results are presented in the form of potential distribution maps and current density vectors in the cell volume. Fig. 2 shows the contour of the potential distribution (X, Y, Z) in an electrolyte during etching of a sample with a textured surface in a horizontal type electrolytic cell.

![Image](contour.png)

**Figure 2.** Potential distribution (color) in an electrolyte during etching of a sample with a textured surface in a horizontal type electrolytic cell.

On the map of the vector field of current densities (Fig. 3) it can be seen that at the edges of the pyramids the maximum component of the current density vector is directed normal to the plane of the plate. The potential difference between the central and marginal regions is more than 20 V. All this leads to the fact that in the intervals between the faces of the textured surface of the region, the formation of pores of different shapes is more intense than in the central parts of the pyramids [9,10].

Also, considering the current vectors in the electrolyte (Fig. 4a) and the velocity isosurface in the electrolyte volume, it can be seen that the greatest value of the currents is achieved at the junctions of the pyramids, where deep macropores with diameters from 0.2 to 2 μm are formed. This is due to the fact that the current lines envelope the pyramidal surface with a crystallographic orientation of (111) and thereby etch sections of the surface of the silicon substrate with a value of (100). Isosurfaces of velocities inside the electrolyte volume showed that the highest values are achieved in the central regions of the substrate. As you move away from the center of the surface along the X, Y axes, a linear decrease in values occurs (Fig. 4b).
Figure 3. Comparison of the contour map of the potential distribution (color) and current density vectors (points) directed along the Z axis with the morphology of the etched textured substrate in a horizontal type electrochemical cell.

Figure 4. Distribution of the line of currents in a limited volume of electrolyte (a) and isosurface of the velocities of fluorine ions (b).

5. Conclusion
Simulation of the field during electrochemical etching showed that its distribution near the silicon-electrolyte interface is determined by the microrelief of the initial surface between the silicon anode and the electrolyte is determined by the microrelief of the initial surface and determines the features of the porous layer formed.

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7. References
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