PAPER REFERENCE S/PI.22 – REVISED VERSION

SELFORGANIZED FORMATION OF CRYSTALLOGRAPHICALLY ORIENTED OCTAHEDRAL CAVITIES DURING ELECTROCHEMICAL PORE ETCHING

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Abstract

The parameter dependence of electrochemically etched pores in silicon is studied. Using HF containing organic electrolytes and backside illumination on moderately doped silicon macropores and octahedrally shaped pores can grow simultaneously. All experimental results can be understood within the framework of the current burst model under the assumption that the system selforganizes and switches the pore morphologies to that mode which optimally consumes the available electronic holes in the reactions. These results can be used to control the pore growth and will be taken as an input for a Monte Carlo simulation to get a quantitative description of the etching processes.

Keywords: Self organization, electrochemical pore etching

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1. Introduction

In the last decade electrochemical etching of semiconductors has been developed as a powerful tool for microstructuring [1]. Especially macropores in silicon allow for aspect ratios of up to 500 and thus to fabricate extremely deep structures, e.g. membranes for biotechnological applications [2]. Additionally the optical properties of the semiconductors can be changed by the pores, e.g. by forming photonic crystals [3] or by enhancement of non-linear material properties [4].

The electrochemically etched pores show a strong crystallographic orientation dependence [4, 5], e.g. in silicon, the (100) surfaces are preferentially dissolved, i.e. they are the pore tips, and the (111) surfaces are most stable against dissolution, i.e. pore walls are mostly (111) oriented. Depending on the etching conditions, pores with extremely different morphologies from the nm to the μ m regime [6, 7] can be etched. Generally, electronic holes are necessary to initiate the etching reaction. In the case of n-type Si, holes can be either created by electrical breakthrough drectly at the interface or photogenerated by illuminating the backside of the sample with NIR-light from where they can diffuse to the pore tips to promote dissolution. In order to control pore etching, e.g. to grow only one specific pore type stable through a complete wafer, a deep understanding of the underlying processes is necessary. Selforganization plays a major role in the formation of electrochemically etched pores, it can define the distance between pores, lead to a self ordering of periodic pore lattices in two and three dimensions, and it defines the composition of different pore types within one sample.

In this paper we will focus on the growth mechanism of octahedral pores in silicon. These are connected chains of (111) bordered cavities ordered along a (100) direction (Fig. 2a). The formation of such cavities is a general feature of semiconductor electrochemistry, e.g. in GaAs tetrahedrons form instead of octahedrons (Fig. 2b) [4]. Experimental data concerning the morphology and the stability

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of such pores will be presented and qualitatively discussed within the framework of the current burst model which has already been successfully applied to explain several other aspects of pore formation in semiconductors. Currently, we are starting to use these conclusions as an input for Monte Carlo simulations to get fully quantitative results.

2. Experimental Setup

All experiments were carried out using a customized etching setup (**Fig. 1**). The ohmic contact to the Si wafer was prepared with InGa and a Teflon etching cell was used. The electrolyte was temperature stabilized at 20 °C and pumped through the cell to avoid inhomogeneities. A custom build potentiostat and an IR-LED-Illumination were computer-controlled to allow for potentiostatic etching conditions and to adjust independently the etching current via the backside illumination. Standard n-Si (CZ) (100)-oriented wafers with a resistivity of 3.5 - 6.5 ? cm were used. The current density varied between 0.5 and 8 mA/cm² and potentials from 1 to 20 V were applied. The ratio between the etching current and current for driving the LEDs was also measured since it almost directly scales to the valence of the etching reaction. The 49 %wt HF was diluted with organic dimethyl formamide (DMF) to result in HF-concentrations of 2 to 6.5 %wt. To change the pH-value of the solution from initially 2.9 to 2.0, HCl (37 %wt) was added in a series of experiments. All samples were broken and the cross sections were analyzed with a Philips XL30 scanning electron microscope to measure the diameter of the octahedrons and the overlap of the octahedrons (**Fig. 3a**). The distance of two adjacent octahedrons was subtracted from their diameter to obtain the overlap.

3. Results

In an initial series of experiments the regime was checked in which octahedral pores can grow. Keeping the other etching parameters constant (U = 4 V, 4 %wt HF in DMF) the etching current was varied between $j = 0 - 1.2 \text{ mA/cm}^2$. Only for small etching currents, i.e. low illumination intensities, octahedral pores grow; at stronger illumination only macropores are found. As can be seen from **Fig. 3b** the octahedral pores vanish after about 15 µm. This coincides with a decrease in the ratio of etching current and illumination current which is plotted logarithmically in the inset at the right side of **Fig. 3b**. For stable macropore growth, i.e. the pore tips grow monotonically towards the illumination source, the distance for the electronic holes to cover by diffusion shrinks in the same manner as pores grow. Lesser and lesser holes are lost due to electron-hole-recombination and illumination intensity is constantly reduced to keep the etching current constant and one expects an exponential increase of the above current ratio. This is found in the region D where no octahedral pores exist. After the pore nucleation A, in phase B the current ratio stays nearly constant and reduces as soon as the octahedral pores start to vanish in phase C. From this behavior one can conclude that the octahedral pores dissolve with a smaller chemical valance than the macropores.

Increasing the applied voltage from 4 V to 8 V and 12 V the octahedral pores grow much deeper with monotonically decreasing density, but applying 20 V through the complete etched area octahedral pores are found without any significant reduction of the density. Additionally the diameter and the overlap of the octahedrons (for the definition see **Fig. 3a**) change significantly with the variation of the applied voltage. As illustrated in **Fig. 4a** the diameter of the octahedral pores decreases and the overlap of the octahedral pores increases with increasing etching potential.

In a last series of experiments the influence of the HF-concentrations for fixed U = 12 V and j = 1 mA/cm² was investigated. The diameter as well as the overlap of the octahedrons increases

with increasing HF concentration (cf. **Fig. 4b**). In contrast to this result, the variation of the pH-value by adding HCl to the electrolyte has no significant influence on the octahedra geometry.

4. Discussion

4.1 Comparison of octahedral and macropore growth

As can be concluded from Fig. 3b, but as well from other experimental results [9], macropores are etched with a larger valence than octahedral pores. The additional hole supply by backside illumination thus favors the growth of macropores. The space charge region which forms around the macropore tips focuses the holes (diffused from the backside) exclusively onto the pore tip leading to a preferential growth at the tip (Fig. 5). The octahedral pores can grow without backside illumination since the necessary holes are generated by avalanche breakthrough at the pore tips as schematically illustrated in Fig. 5. In the case of Fig. 3b, the etching bias is relatively low and therefore, after a certain depth, ohmic losses in the electrolyte make sure that the etching potential available at the Si-HF-interface is too low to further induce avalanche breakdown. As a result of this, octahedral pores stop to grow. Increasing the overall etching potential will therefore stabilize and favor octahedral pore growth with explains the results of Fig. 3b and 4a. Silicon can be dissolved via oxide formation and dissolution with a valence of 4 and via direct dissolution with a valence of about 2 [7, 8]. So macropores most probably grow with a large fraction of oxide formation, leading to smooth structures due to the electropolishing effect of isotropic oxide formation. Octahedral pores grow by direct silicon dissolution which allows for a strong crystallographic anisotropy, i.e. preferential dissolution of (100) surfaces and enhanced passivation of (111) surfaces. These are exactly the growing conditions of mesopores [8, 9], so the octahedral pores seem to be a special kind of mesopores.

4.2 Model for the octahedral pore growth

In silicon as well as in III-V compounds octahedral respectively tetrahedral pores have never been found directly starting from the surface of the sample. So some kind of diffusion limitations seem to be essential for the formation of cavities. A possible scenario for the growth of interconnected octahedrons is illustrated in Fig. 6 An isotropic dissolution at the pore tip (a, b) proceeds until a diffusion limitation for the chemical reactions at the pore walls starts (c). At this point the surface can start to passivate since the local current density at the pore walls is no more at maximum. The (111) surfaces, which are faster chemically passivated, stop to dissolve which leads to the octahedral shape (d). When too much surface gets passivated the electrical power $U_{etch}*I_{etch}$ which is carried through the Si-electrolyte-interface decreases. To stop this trend a new octahedron forms at one of the tips of the previous octahedron and the cycle starts again (e). Combining the experimental results for the overlap of adjacent octahedrons in Fig. 4a and 4b and taking into account that the electrical field strength is the decisive parameter to allow for the necessary avalanche break through the experimental results are consistent with the assumption that a new octahedra starts, as soon as a critical electrical field strength at a pore tip is reached. This field strength is determined by the xtual curvature at the (100) cavity tip and the applied etching potential as schematically illustrated in Fig. 7. Increasing the etching potential the necessary curvature is smaller (Fig. 7b,c) and a new cavity can form earlier which increases the overlap of the octahedrons.

5. Summary

The experimentally determined parameter dependence for the formation of macropores and octahedral cavities can be understood as a competition between direct silicon dissolution and dissolution via oxide formation and dissolution. Depending on the hole supply, the choice of the electrolyte to control the rate for oxide formation, and the HF concentration to allow for silicon oxide dissolution, the system favors that chemical process by selforganization which allows for the largest electrical power transport through the silicon-electrolyte interface.

This qualitative model will be the starting point for a Monte Carlo simulation to get a more quantitative understanding of the underlying selforganization mechanisms, to determine the dependence of the pore morphologies on the etching conditions, and thus to allow for a better control of the pore formation.

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Fig. 1: Experimental setup: An anodic bias is applied on a silicon wafer in contact with a HF containing electrolyte. Additionally, a back side illumination can be used to increase the concentration of holes in a n-Si wafer. Illumination intensity, electrolyte temperature, and applied voltage are computer controlled.

Fig. 2: The formation of cavities with crystallographically oriented walls is a general feature of anodically etching of semiconductors under certain etching conditions. (a) Using back side illumination and organic DMF electrolyte with 4 wt% HF so called macropores and octahedral pores with (111) walls can grow simultaneously. (b) In GaAs only the (111) B (Ga-rich) walls are stable against electrochemical dissolution; thus tetrahedrons are formed.

Fig. 3: (a) The walls of octahedral pores in Si are (111) surfaces. The diameter and distance of the octahedra depend strongly on the etching conditions. (b) After a nucleation phase A) in B) macroand octahedral pores grow simultaneously until in C) the octahedrons die out and D) stable macropore growth starts. These phases clearly show up in the inset which is a plot of $\ln(I_{etch}/I_{illumination})$ as a function of etching time.

Fig. 4: The minimal, average, and maximal octahedron diameter and overlap (cf. Fig. 3a) depend significantly on (a) the applied etching potential and (b) the HF concentration in the organic electrolyte.

Fig. 5: For octahedral pores the necessary electronic holes are generated by avalanche break through at the tips while for macropores photo generated holes are necessary.

Fig. 6: Schematic drawing of the assumed formation mechanism for octahedral pores: As long as no diffusion limitations due to the long chains of octahedrons exist, the cavities grow isotropically (a) with a local current density *j* leading to an increase of surface *A* and thus to an increase of the current I_{Pore} (b) until this current is limited by diffusion (c). The difference in passivation kinetics on (100) and (111) surfaces (aging) will stop the etching of the (111) surfaces and focus the dissolution to the octahedra tips (oriented in (100) direction) leading to a reduction of the etched area within the octahedra (d). Thus it becomes favorable to start a new octahedron at one tip (e).

Fig. 7: Electrical field strength is the driving force to generate holes by avalanche break through which are necessary for the electrochemical formation of octahedral cavities. (a) Increasing the cavity diameter by isotropic dissolution (between time t_1 and t_2) will reduce the curvature of the cavity and thus reduce the electrical field strength. As soon as at a time t_3 the preferential dissolution of the (100) tips starts, the curvature can increase again. Assuming that a critical field strength is necessary to start a new cavity the curvature of the octahedral tips, at which a new octahedron must start, can be smaller when increasing the externally applied potential (b, c).

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(a)



(b)

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