In-situ monitoring of the electrochemical growth of nanoporous silica

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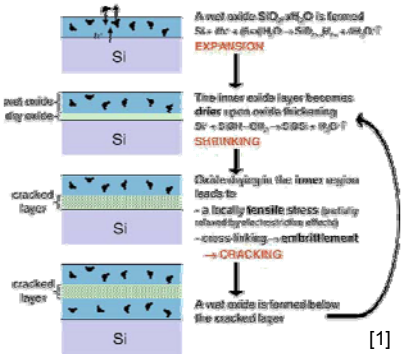
1. Introduction

Galvanostatic anodizing of silicon in hydrofluoric acid solutions results in silica formation and subsequent dissolution. This is accompanied by periodic voltage oscillations. It is generally accepted that the silicon electrode surface is divided into self-oscillating micro domains that can be synchronized to create macroscopic oscillations [1]. Under sufficiently high current density conditions, anodizing leads to the formation of a nanoporous silica film.

The Expansion-Shrinking-Cracking (ESC) model has been proposed by Chazalviel et al. [2] to describe the growth of micrometer thick silica films in basic electrolytes. The model is based on their observation of stratified structures in such silica films.

Voltage and curvature periodic oscillations are observed during the galvanostatic formation of nanoporous silica in acidic electrolyte. Can it be explained by the ESC model ?

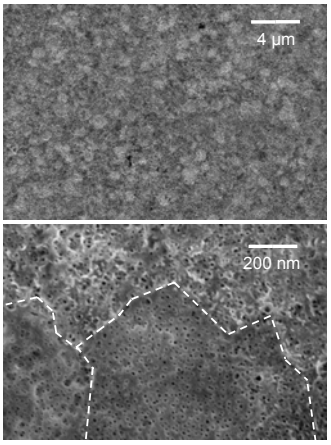


[1]

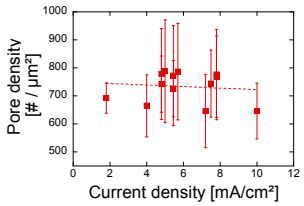
2. Experimental

Silicon : (100)-oriented p-Si wafers (5-15Ωcm). 200µm thick wafers are double-side polished and coated on one side with LPCVD Si_3N_4. Electrolyte : 0.025M HF, 0.025M NH_4F, 0.0975M NH_4Cl (pH 3). Temperature : 18-20 °C. Current density : from 3 to 9 mA/cm². Electrical contact : PtSi. Oxide surface inspected by SEM. Oxide thickness measured ex-situ by spectroscopic Ellipsometry. Sample curvature measured by Multi-Beam Optical Sensor [3].

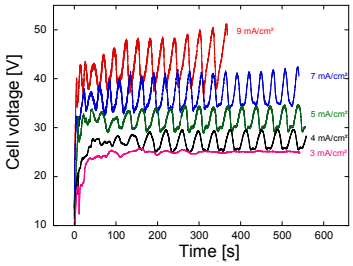
3. Surface morphology of nanoporous silica

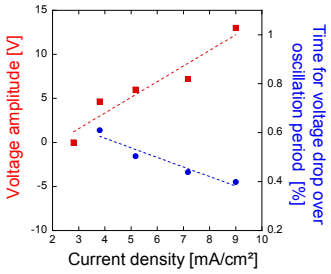


- The silica films surface is divided into areas of high and low roughness (about 1µm in size)
- The pore diameters vary from 7 to 20 nm. Smaller pores are on flats areas and bigger pores on rough areas.
- The silica film thickness varies between 30 and 50 nm and is independent of the anodizing time.
- The current density does not significantly influence the pore density.



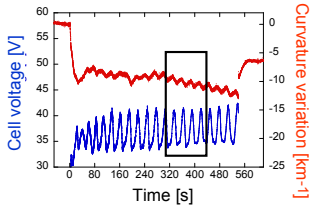
4. Voltage oscillations



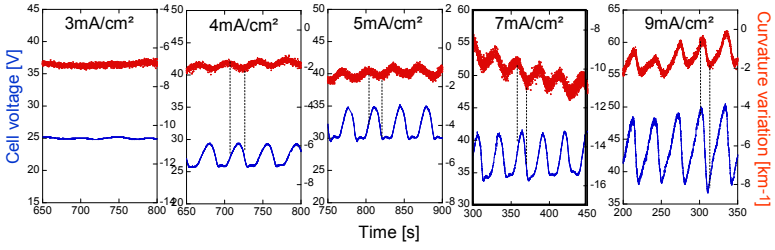


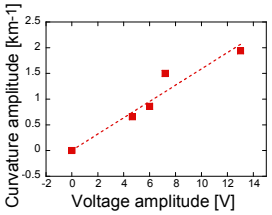
Periodic oscillations appear upon increasing the current density. The higher the current density, the higher the amplitude of the voltage oscillation and the higher the oscillation asymmetry.

5. Curvature oscillations



- Initial curvature increases in compressive direction due to the formation of SiO_2.
- Instantaneous tensile curvature variation when current is stopped.
- Increase of the amplitude of the curvature oscillations with the applied current density

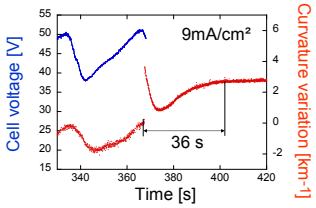




- Curvature oscillations and voltage oscillations synchronize with increasing current density
- The amplitude of the curvature oscillations seems linearly related to the amplitude of the voltage oscillations.
- At 9 mA/cm², two distinct slopes are present during the stage of increasing voltage and curvature.

Domain synchronization scales with current density

6. Open circuit investigation

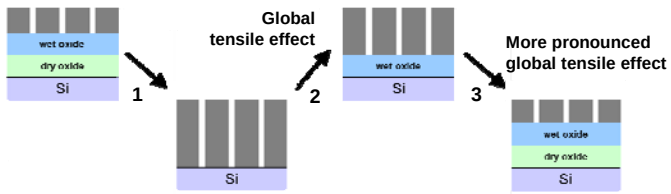


If anodizing is stopped when the curvature reaches its maximum, an abrupt curvature decrease occurs before chemical silicon oxide dissolution by the hydrofluoridric acid.

7. Discussion

To link the present results to the ESC model one should keep in mind that the electrolyte is strongly acidic and will continuously etch the formed silica. One voltage or curvature oscillation should correspond to one cycle of the model.

It seems possible to explain the present results with the ESC model assuming that the silica undergoes a morphological transition forming nanoporous silica with compressive internal stresses.



1. CRACKING
Voltage abrupt decrease
curvature abrupt increases in compressive direction

2. EXPENSION
Voltage slow increase
Curvature slow increases in tensile direction

3. SHRINKING
Voltage fast increase
curvature fast increases in tensile direction

8. References

[1] J.-N. Chazalviel, F. Ozanam, *Electrochimica Acta* 55 656-665 (2010)

[2] J.-N. Chazalviel, R. Cortès, F. Maroun, F. Ozanam, *Phys. Status Solidi A* 206, No 6, 1229-1234 (2009)

[3] Q. Van Overmeere, J.-F. Vanhumbeeck, J. Proost, *Rev. Sci. Instrum.* 81, No 4, 045106 (2010)

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