

## Modeling of the electrochemical anodization of silicon: state-of-the-art and perspectives

Vitali Parkhutik

Department of Materials Science, Technical University of Valencia, Cami de Vera s/n, 46022 Valencia, Spain

### INTRODUCTION

The purpose of this work is to review recent advances in understanding the electrochemical kinetics of silicon in different electrolytes and studying solid-state products of electrochemical reactions.

Anodic polarization of Si yields a formation of porous silicon (pSi), silicon anodic oxides (SAO) and results in Si electropolishing, depending on the experimental conditions. Each process finds important practical applications while their scientific backgrounds still remain to be discovered.

*Porous silicon* (pSi) is formed in HF-based electrolytes ensuring local pit-like electro-dissolution of silicon. This material attracts much attention due to emerging applications in electronics, optics and chemistry.<sup>1</sup> Very recently biodegradability of pSi and its photo-sensitizing properties has given rise to biomedical applications of this material. Within the family of porous silicon films one has to distinguish nano- meso y macro-porous films, each requiring specific formation conditions.

There have been a number of models interpreting the growth of porous silicon films.<sup>2</sup> Some of them yield quite realistic view of the kinetics of the pore growth. Figure 1 shows how the diameter of the pores is changing if the polarization voltage sharply increases

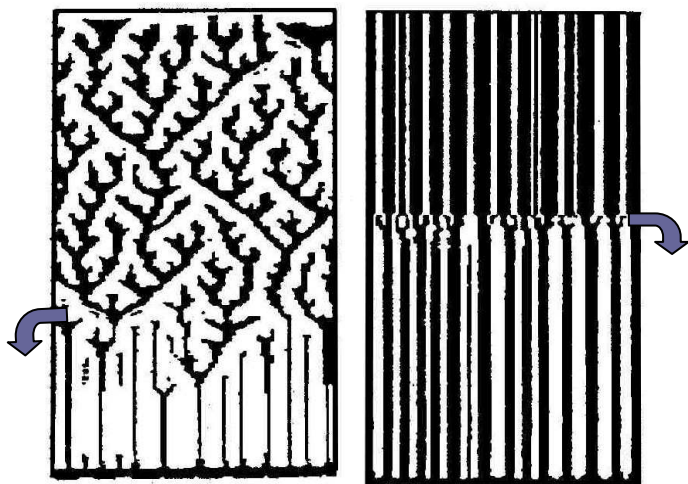


Figure 1. Theoretical modeling of morphology change of porous silicon at sharp increase of anodic voltage (at the moments shown by arrows)<sup>2</sup>

However, neither of existing pSi models is complete enough to ensure, at present, a comprehensive insight into important matters related with the formation of pSi films.

*Anodic oxides of silicon* formed by anodic polarization in aqueous and non-aqueous solutions of acids and salts (e.g.  $\text{KNO}_3$ ) has attracted much research in sixties due to the hope to obtain high quality gate dielectrics for MOS transistors.<sup>3</sup> However, excessive density of surface states at Si/oxide interface hindered the interest to Si anodic oxides. There have been developed just few models regarding the growth of anodic oxides which were not

advanced enough to explain the features of the oxide growth and its properties.

Finally, anisotropic electro-dissolution of Si in alkaline solutions is a basic process for deep etching of Si and MEMS applications, though the knowledge accumulated till now has remained mainly empiric.

Analyzing the state of the art in the understanding the mechanism of the electrochemical anodizing of Si the following can be pointed out.

1. All three cases mentioned above are considered separately and modeled independently. No universal point of view on Si electrochemistry has been introduced.
2. Weak or no theoretical background is provided to support existing model assumptions. The existing models lack, very often, realistic physical-chemical background that limits their utility.
3. No correlation with other electrochemical processes yielding porous structures growth (f.i. pitting corrosion of aluminum or porous oxide growth on the same) has been done, though this might be very useful to obtain better understanding of fundamental issues of porous structures growth.

### NEW ISSUES IN MODELLING THE ELECTROCHEMICAL KINETICS ON SILICON

Recently there have emerged new experimental data which, most probable, would serve to introduce breakthroughs into the Si electrochemistry. Among them:

*Oscillatory electrochemical reactions.* Several research groups independently have registered an oscillatory electrochemical kinetics on Si in contact with fluoride-based electrolytes. Oscillations of anodic current or voltage are sensitive to the temperature of electrolyte, its viscosity, crystallographic orientation of Si wafers and other experimental variables. Interpretation of this behavior is rather different, ranging from current-burst model of cyclic change of thickness of oxide layer developed by Foll et al.<sup>4</sup> till multilayer oxide growth model by the present author.<sup>5</sup> In any case oscillatory anodization kinetics could only be understood taking in mind both oxide growth and its local dissolution, thus making bridge between classic porous silicon growth and anodic oxide formation.

*Accumulation of mechanical stress at Si/SiO<sub>2</sub> interface.* Application of Small Angle X-ray Scattering technique to the analysis of interface between SiO<sub>2</sub> and Si has revealed an existence of highly stressed layer of approximately 10-20Å at the interface where SiO<sub>2</sub> density achieves 2.5 g/cm<sup>3</sup> while the stoichiometric silicon dioxide gives only 2.2 g/cm<sup>3</sup>. Further evidence of this stress has been obtained recently in micro-Raman studies of pSi/c-Si interface.

These are other data serve to suggest universal and comprehensive model of electrochemical kinetics of Si.

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