



3D simulations of ordered nanopore growth in alumina



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ABSTRACT

Anodization is an inexpensive and simple method for obtaining oxide layers on metals. When performed in certain parameter regimes these layers are nanostructured and can be used as scaffolds in manufacturing nanodevices. There is much dispute in the scientific community concerning the mechanism of anodization. Two models are most prominently featured in literature: Field Assisted Flow and Field Assisted Dissolution. We present a cellular automata implementation of the Field Assisted Dissolution model of anodization. In our work we provide evidence that this model yields the predicted hexagonally ordered porous layers that is in qualitative agreement with experimental work.

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1. Introduction

Highly ordered anodic alumina is considered a very good and cheap material for the fabrication of scaffolds for low dimensional nanomaterials [1]. The structure of ordered anodic aluminum was first discovered by Keller, et al. in 1956 [2]. An experimental regime to obtain hexagonally ordered nanopores in aluminum oxide was discovered by Masuda in 1995. [3]. Experimental progress has been rapid but the explanation of the mechanism of pore formation and propagation is a subject of debate. Two models most prominently featured in literature of the subject are Field Assisted Flow (FAF) and Field Assisted Dissolution (FAD).

The Field Assisted Flow model was initially proposed by Garcia-Vergara, et al. [4]. Experimental evidence pointing to this model were presented by the very same group [5]. In this model the proposed mechanism of pore formation is the displacement of oxide material in the formed layer. The driving force of the process is assumed to be pressure that arises due to the difference between the volume of the created oxide and the used metal (the Pilling-Bedworth factor). The plasticity of alumina allows to relieve the aforementioned stress in the layer via dislocating layer material. This dislocation leads to the formation of a self organized nanoporous structure. The topic of stability of such structures in the Field Assisted Flow model has been further explored by Singh, et al. [6]. The former of these papers establishes a two

dimensional mathematical description of the Field Assisted Flow model and uses weak nonlinear analysis to predict the stability of pores. The authors conclude that weak nonlinear analysis predicts the emergence of pores in this model. However, deep pores cannot be treated as small perturbations of planar surfaces and the authors encourage further research into the subject. The work of Sheintuch and Smagina [7] takes a similar model to the one used by Singh, et al. [6]. The authors ultimately arrive at the evolution equation for the metal-oxide interface that is in the form of the Damped Kuramoto-Sivashinsky equation. Again a weak nonlinear analysis of the model suggests that a porous structure is stable and simulations of the obtained equations result in porous structures. However, two factors remain questionable in this model: it deals only with the initial stage of porous growth and the model is two dimensional. A paper by Gomez and Paris [8] analyzes the Damped Kuramoto-Sivashinsky equation in unusual two dimensional settings and in three dimensions. The results obtained by Gomez and Paris found asymptotic states for all two dimensional cases similar to those obtained for square geometries. However, the authors consistently found chaotic asymptotic states for the three dimensional Damped Kuramoto-Sivashinsky equation. This result implies that in a three dimensional environment a stable porous state for the Field Assisted Flow model may not exist.

The second most commonly used model of anodization of aluminum is Field Assisted Dissolution. First suggested in 1959 by Hoar and Mott [9] this model explains pore formation by assuming that reaction rates are greatly altered in the presence of a strong electric field. In this model several noteworthy phenomena are assumed to take place:

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1. Dissolution of oxide material at the solvent-oxide interface
2. Dissociation of solvent particles at the solvent-oxide interface
3. Anion migration in the oxide layer
4. Metal oxidation at the metal-oxide interface

The physical mechanism of action of the electric field proposed by O'Sullivan and Wood [10] is as follows. The key assumption in the Field Assisted Dissolution model is that the rates of oxide dissolution and solvent dissociation are significantly affected by the electric field. Both oxide material and water that is used as a solvent are highly polar. In the presence of a strong electric field the particles get stretched hence weakening the chemical bond. This weakened bond has a greater chance of breaking and hence reactions involving breaking this bond are accelerated in high electric field. The formation of a porous structure is explained as follows. Initially a flat barrier layer of oxide is formed. The layer is then perturbed in some way. For example surface defects or naturally occurring fluctuations can be a source of a perturbation. The perturbation leads to a situation in which some parts of the layer are exposed to a higher electric field than other parts. Higher electric field yields more oxide dissolution and anion incorporation into the layer. In its turn it initiates the pore growth and decreasing the distance between the metal and solution increases the field at the pore bottom even more. A steady state of pore growth is achieved when the overall rate of metal oxidation equates the rate of oxide dissolution. Experimental data is also in line with the predictions of the Field Assisted Dissolution model as shown in works of Garcia-Vergara, *et al.* [11,12]. Coupling the model with a Laplace equation Parkhutik and Shershulsky [13] were the first to show a linear relationship between applied voltage and pore spacing. The aim of this work is to verify if a stable porous structure can actually be obtained using the Field Assisted Dissolution model.

2. Theoretical model

We base our implementation of the Field Assisted Dissolution model on the work of Parkhutik and Shershulsky [13]. The basic equation for the electric field in the oxide is the Poisson equation:

$$\nabla^2 \varphi = \frac{\rho_f}{\epsilon} \quad (1)$$

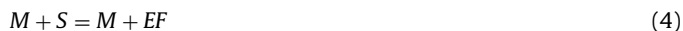
with boundary conditions:

$$\varphi_{Ox \setminus S} = 0 \quad (2)$$

$$\varphi_{M \setminus Ox} = U_{M \setminus Ox} \quad (3)$$

where $\varphi_{Ox \setminus S}$ is the potential at the oxide-solvent interface, $\varphi_{M \setminus Ox}$ is the potential at the metal-oxide interface and $U_{M \setminus Ox}$ is the voltage applied to the system. Following Parkhutik and Shershulsky we assume the electric field does not penetrate into the solvent which is much better conductor than the layer itself. To solve the resulting equation for the electric field we use the Random Walk [14] approach. We design a probabilistic, asynchronous cellular automaton on a cubic lattice with Moore connectivity and periodic boundary conditions along two axes parallel to the surface. Constant boundary conditions are applied for the third axis. We use the block-synchronous method presented by Olga Bandman [15,16] in our approach to parallelization. Our model consists of 5 states that a cell can be found in. These states are: *M* representing the bulk metal, *S* representing the electrolyte, *OX* representing the metal oxide, *A* representing an anion enriched portion of the metal oxide and *EF* whose flow through the system simulates the electric field. States *OX*, *A* and *EF* are called *oxide-like* states since they form the entirety of the oxide layer. The rules to change the states in the model may be divided into three sub categories: reaction type rules,

diffusion type rules and surface diffusion type rules. A hypothetical rule and the way to interpret it is given in the following example.



The interpretation of this rule is as follows: An *M* particle in site A reacts with an *S* particle in site B yielding an *M* particle in site A and an *EF* particle in site B. In the above reaction, we omit an explicit notation for the sites A and B, as in the course of the simulation they correspond to a random pair of neighboring sites chosen with the algorithm detailed thereafter. The reaction-like rules we use are as follows:



Each reaction-like rule has a unique probability and can be viewed as a representation of a certain physical or chemical process. These processes are passivation of a metallic surface in an aggressive environment in case of rule 5. Dissolution of oxide material 6, dissociation of solvent 7. The probabilities of rules 6 and 7 sum up to 1. Oxidation of metal 8 and having voltage applied to the system 9. This set of rules covers all the most important features of the Field Assisted Dissolution model.

Diffusion type rules describe the random walk of *EF* particles in the oxide layer and are used to model the electric field:



These rules have a constant probability of 1. Surface diffusion rules describe surface tension on the oxide/solvent interface.



These position swaps occur always when *OX* or *A* find a *S* site that has more *oxide-like* neighbors than their current position. In case of finding a *S* site with less neighbors than the current position a swap is still possible and is governed by a power law depending on the neighbor-neighbor bond number change between the current and would be positions.

3. Results and discussion

All of our simulations are conducted in systems of size 300(X-direction) by 300(Y-direction) by 600(Z-direction) sites. The starting conditions are a flat metallic surface to 580 sites in the Z direction and solvent above it. The probabilities used for the five reaction like rules are:



First in Fig. 1 we show the side view of the result of our simulations. An elongated porous structure is visible. More details about the structure can be obtained from further figures.

In Fig. 2 we show the profile of *oxide-like* particles along the Z-axis of our simulated system.

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