

Biomaterials in Microsystems: An Investigation of the Effect of Parent Ti Microstructure on the Morphology of Nanostructured Titania

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Abstract:

Nano-structured titania (ns-TiO₂) has many desirable properties for integration into biological systems and nano/micro electrical mechanical systems (N/MEMS). Ns-TiO₂ is being considered for applications ranging from catalyst for organic decontamination, cell scaffolds for implantable devices and sensing elements for detection of gases and biological macromolecules.

One promising route for implementing ns-titania into N/MEMS devices is by reacting titanium films with aqueous hydrogen peroxide (H₂O₂) solution. Hence the effect of parent Ti microstructure and H₂O₂ solution on the morphology ns-titania produced needs to be understood. This work investigates the kinetics of the above reaction using an electro-oxidation method. The effect of parent Ti film thickness, deposition rate of Ti films, H₂O₂ concentration and temperature on the reaction kinetics was investigated.

Introduction:

There are two main objectives for researching the reaction of ultra-thin titanium metal films (< 0.5 μm) with H₂O₂ solution to form nano-structured titania (TiO₂). The first is to understand the kinetics of the reaction and to determine the rate-limiting step. The second is to evaluate the morphology of the ns-titania as related to the reaction conditions and the microstructure of the parent Ti films.

We found two reaction kinetics depending on thickness of the parent Ti film. For films less than 50 nm thick, the kinetics are interface-reaction controlled. For thicker films, the reaction is controlled by the diffusion of Ti through an intermediate gel layer. The titania gel layer has a porous sponge-like morphology and is amorphous. Upon annealing at 300°C, the gel crystallizes into anatase nano-crystals about 5-25 nm in diameter. The ns-titania layer was evaluated using UV-Vis, XRD, AFM, and SEM.

Procedure:

The main method that evaluates the progress of the reaction is electro-oxidation. A thin film of Ti is

evaporated onto a glass substrate in the form of a circuit. The circuit is closed using a Digital Multimeter to record resistance changes as the reaction takes place. The circuit on the glass slide is then partially submerged into a beaker of 180 ml of 10% H₂O₂ that has been heated to 80°C. A lid with a slit cut out for the glass slide covers the beaker, and PDMS is used to seal the remaining incongruities between the slit and the slide. Figure 1 shows a diagram of this setup.

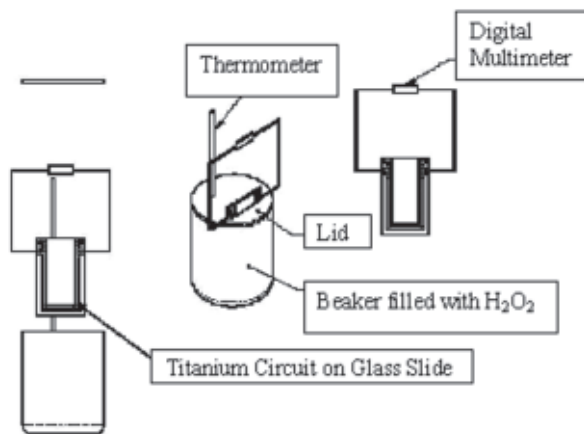


Figure 1: Diagram of the Electro-Oxidation Method.

Using the electro-oxidation method, the reaction is evaluated as a function of time, temperature, parent Ti film thickness, H₂O₂ concentration, and deposition rate of the Ti film.

Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD) and UV-Visible Spectroscopy are implemented to evaluate the morphology of the ns-titania.

Results and Conclusions:

For the electro-oxidation data, refer to the table of graphs in Figure 2. The thicker Ti films (> 0.5 μm) proceed by a diffusion-limited reaction kinetic, and the thinner Ti films (< 0.5 μm) proceed by an interface-limited reaction kinetic (Figure 2A). The lower concentrations of H₂O₂ (5% for 50 nm and 5, 10% for 200 nm) proceed by the diffusion-limited kinetic, and the higher concentrations proceed by the interface-

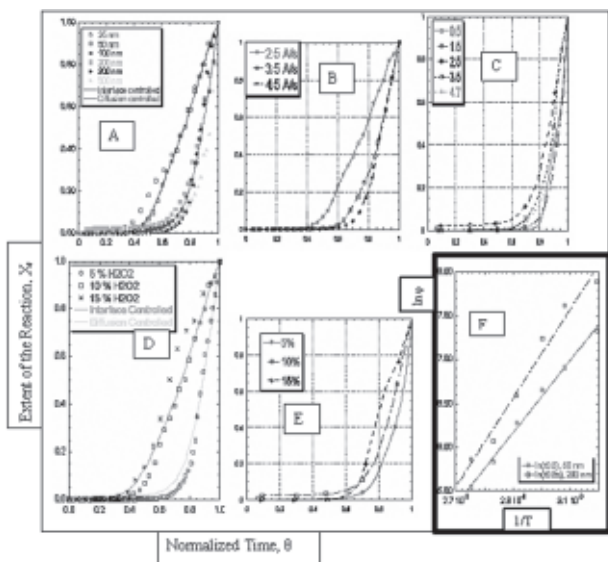


Figure 2: Table of Graphs.

limited reaction kinetic. Figure 2D is the graph for the 50 nm samples and 2E is the graph for the 200 nm samples. For the slower deposition rates of the 50 nm samples, the reaction proceeds by the interface reaction kinetic (Figure 2B). All of the 200 nm samples proceed by the diffusion-limited reaction kinetic when varying the deposition rate (Figure 2C). The normalization method for the electro-oxidation data is explained in Figure 3.

Normalization	Activation Energy Analysis
At $\frac{dR}{dt} = 0$, $t = t_{\infty}$ and $R(t_{\infty}) = R_{\infty}$	$\phi = \phi_0 e^{-\frac{E_a}{kT}}$
Extent of the reaction, $X_i = \frac{R(t) - R(0)}{R(t_{\infty}) - R(0)}$	$\ln \phi = \frac{E_a}{kT} + \phi_0$
Normalized Time, $\theta = \frac{t}{t_{\infty}}$	Figure 3: Calculations.

As the Ti ions and the H_2O_2 react, they form an amorphous gel layer through which the molecules must diffuse for the reaction to take place. Which molecule diffuses is unknown. At the thinner films, the gel layer is so thin that the rate-limiting step is the actual binding of the H_2O_2 molecules to the Ti (IV) ion, or the interface control. At thicker films, the diffusion of the molecules through the gel layer is the rate-limiting step, or the diffusion control.

By varying the temperature, it is possible to find the activation energy required for the reaction to occur (Figure 2F). In Figure 3, the way the activation energy graph is plotted is explained. The activation energy for the interface controlled reaction kinetic is exactly double what Sever theorized the activation energy of one H_2O_2 molecule to bind to one Ti (IV) ion [1]. Samuni postulated that the reaction mechanism might

take place between a Ti (IV) ion and more than one molecule of H_2O_2 [2]. It is likely that the mechanism for the interface-controlled reaction occurs with the binding of two H_2O_2 molecules to one Ti (IV) ion.

The XRD and UV-Vis data is only used to verify that the samples we are creating actually are titania, and that upon annealing the amorphous TiO_2 at $300^{\circ}C$, we were forming an anatase crystal structure. The SEM and AFM photos were used to evaluate the morphology of the ns-titania, as formed, as a function of the thickness of the parent Ti film.

In Figure 4, it is evident that for thicker Ti films, the ns-titania has a porous, sponge-like morphology. For thinner Ti films, the ns-titania has a porous, grain-like morphology.

Future Work:

The future work for this project includes optimizing the process conditions to implement ns-titania into actual devices. In this work unpatterned ns-titania films are formed. However, implementation of ns-titania into practical devices requires the use of patterning of ns-titania films. Hence further work should study the feasibility of different materials such as silicon nitride and silicon dioxide as masks. Also, the effect pore size of the ns-titania needs to be quantified using gas-adsorption techniques. This is critical for application of ns-titania as 'active' components in devices for macromolecular separation.

Acknowledgments:

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References:

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- [2] A. Samuni, J. Phys. Chem. 1972, 76, 634.

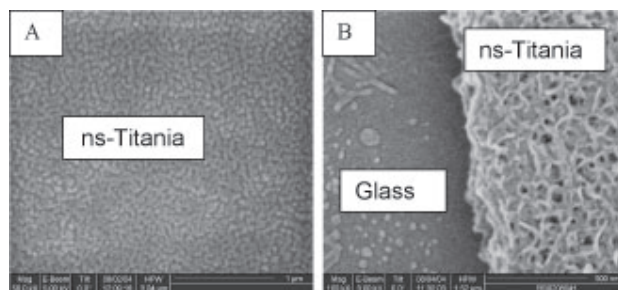


Figure 4: SEM: A, 100 nm parent Ti film; B, 500 nm parent Ti film.